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Thermodynamics of Heterogeneous Polymers and Their Solutions[1]

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The statistical mechanical treatment previously applied to homogeneous polymer solutions has been extended to heterogeneous polymers composed of numerous molecular species differing in polymer chain length. Entropies of mixing with solvent are derived with reference to three standard states: the oriented pure components, the disoriented pure components, and the disoriented mixture of species. The entropy of mixing with respect to the last-mentioned state is identical with that previously derived neglecting polymer heterogeneity. Upon introducing a van Laar heat of mixing term, expressions for the partial molal free energies are derived. These should be reasonably correct in view of the satisfactory agreement between observed solvent activities in polymer-solvent solutions and theory, as shown by Huggins. The relationships should be useful not only in dealing with solutions, but also in equilibria involving heterogeneous polymers in the absence of solvent. The thermodynamic equations are applied to the problem of equilibrium in the range of partial miscibility for solvent-heterogeneous polymer systems. The requisites for efficient fractionation of high polymers are discussed. The efficiency of separation depends on the ratio of the volumes of the supernatant and the precipitated phases. In order to attain a high value for this ratio, very dilute solutions must be employed. The higher the molecular weight at which separation occurs the greater the dilution required for the same sharpness of separation. The free energy expressions are also applied to the formulation of equilibrium constants to be employed in reversible polymerization-degradation processes. It is shown that concentrations should be expressed in moles per unit volume in the equilibrium constant. The equilibrium state for a polyfunctional condensation, considered as a reaction between functional groups, is not affected by the polymeric nature of the reacting species; the position of equilibrium should be the same as is found for analogous monofunctional reactants under the same conditions.

INTRODUCTION

SOLUTIONS of high polymers have been known for some time to behave anomalously[2–4] with respect to the ideal solution laws as originally set up for solutions of simple molecules. These apparent anomalies in thermodynamic and related behavior have been largely cleared up by statistical mechanical treatments[5–7] of high polymer solutions which have appeared in the last few years. These treatments are based on the following physical approximation: The liquid mixture composed of long chain polymer and monomeric solvent molecules is assumed to conform to a pseudo-lattice structure, each cell of which may be occupied either by a molecule of solvent or by an element of the chain (segment) equal in size to a solvent molecule. Proceeding from this concept, it has been

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[2] W. Ostwald, Kolloid Zeits. **46**, 248 (1928).
[3] K. H. Meyer and R. Lühdemann, Helv. Chim. Acta, **18**, 307 (1935).
[4] K. H. Meyer, *Natural and Synthetic High Polymers* (Interscience Publishers, Inc., New York, 1942), pp. 582–595.
[5] M. L. Huggins, J. Phys. Chem. **46**, 151 (1942); Ann. N. Y. Acad. Sci. **43**, 1 (1942); J. Am. Chem. Soc. **64**, 1712 (1942).
[6] P. J. Flory, J. Chem. Phys. **10**, 51 (1942).
[7] A. R. Miller, Proc. Camb. Phil. Soc. **39**, 54 (1943).

possible to derive by an approximate mathematical procedure the following expression[6] for the entropy of mixing n solvent with N polymeric solute molecules (initially in random configurations in the pure state) where

$$\Delta S_{\text{mixing}} = -k[n \ln v_1 + N \ln v_2]; \qquad (1)$$

v_1 and v_2 are the volume fractions of the components, solvent and polymeric solute, respectively. This expression differs from the one representing the so-called "ideal" solution in that *mole* fractions are replaced by *volume* fractions. Inasmuch as the ideal solution law can be derived theoretically only for solutions of equal-sized species, where volume fractions equal mole fractions, the conventional ideal solution is seen to be included as a special case of Eq. (1).

Although certain limitations on this statistical treatment as applied to polymer solutions have become apparent,[8] sufficient agreement with experiment has been obtained[5, 6, 9, 10] to encourage extension of this method of attack. It is the purpose of the present paper to extend the previous statistical mechanical method to heterogeneous polymers and their solutions in which the polymer constituent is actually a mixture of many species differing in length, or molecular weight. The resulting equations afford a basis for dealing with chemical equilibria involving interconversion of the polymer species. They can also be applied to the problem of fractionation of polymers, as, for example, by fractional precipitation from solution.

DERIVATION OF ENTROPIES OF MIXING

The procedure closely parallels that which has been given previously for a polymer consisting of a single species. The pseudo-lattice for the solution is to be filled by successively adding the polymer molecules to it, then filling in the vacant cells with molecules of solvent. Suppose that $j-1$ polymer molcules previously have been assigned locations in the lattice. The number of unoccupied sites in the lattice will be given by

$$n_0 - \sum_{n=1}^{j-1} x_i$$

where n_0 is the total number of lattice sites and x_i is the number of segments in the ith molecule ($i<j$). This factor will represent the number of sites available to the terminal segment of the jth molecule to be added to the lattice. The cell to which this first segment is assigned will be surrounded by γ-sites for the second segment, where γ is a "coordination number" for the lattice. Some of these may be occupied by segments of molecules previously added to the lattice. The expected number of available sites for the second segment of the jth molecule can be expressed therefore as the product of γ into the fraction of all lattice sites which are not occupied by previously added segments of molecules;[6] this product is given by

$$\gamma\left(n_0 - \sum_{i=1}^{j-1} x_i - 1\right) \Big/ n_0.$$

Of the γ-lattice sites surrounding the second segment, one is occupied by the first segment. The expected number of sites available to the third segment, therefore, will be

$$(\gamma-1)\left(n_0 - \sum_{i=1}^{j-1} x_i - 2\right) \Big/ n_0.$$

Similarly for the ξth segment of the jth molecule the expected number of available sites will be

$$(\gamma-1)\left[n_0 - \sum_{i=1}^{j-1} x_i - (\xi-1)\right] \Big/ n_0. \qquad (2)^{11}$$

The number (or expected number) of configurations available to the jth molecule as a whole can be obtained by combining the factors given above for the expected numbers of sites available to each segment. The resulting ex-

[8] Paper presented before the Division of Physical and Inorganic Chemistry at the Pittsburgh Meeting of the American Chemical Society, September 6, 1943. To be published shortly.

[9] M. L. Huggins, Ind. Eng. Chem. **35**, 216, 980 (1943); Ann. N. Y. Acad. Sci. **44**, 431 (1943).

[10] G. Gee and L. R. G. Treloar, Trans. Faraday Soc. **38**, 147 (1942).

[11] The term $(\xi-1)$ in these expressions may be open to objections on the grounds that segments of the jth molecule are not to be considered the equivalent of segments of other molecules which may locate any place in the lattice. In any event, its contribution to the term is insignificant, and could be omitted entirely. It has been included here for the reason that it simplifies reduction of the subsequent equations.

pression becomes

$$\nu_j=\frac{1}{\sigma}\left[n_0-\sum_{i=1}^{j-1}x_i\right][\gamma/(\gamma-1)]$$
$$\times\prod_{\xi=2}^{x_j}\left[\left(n_0-\sum_{i=1}^{j-1}x_i-\xi+1\right)(\gamma-1)\Big/n_0\right].$$

The symmetry number σ of the polymer molecules usually may be taken equal to two, in consideration of the equivalence of the ends of the molecule. Replacing $\gamma/(\gamma-1)$ by unity in the second factor in brackets in the equation given above,

$$\nu_j=[n_0/\sigma(\gamma-1)]\prod_{\xi=0}^{x_j-1}$$
$$\times\left[\left(n_0-\sum_{i=1}^{j-1}x_i-\xi\right)(\gamma-1)\Big/n_0\right]$$
$$=\frac{1}{\sigma}\left(\frac{\gamma-1}{n_0}\right)^{x_j-1}\left(n_0-\sum_{i=1}^{j-1}x_i\right)!\Big/$$
$$\left(n_0-\sum_{i=1}^{j}x_i\right)!. \quad (3)$$

The total number of configurations available to the system of N polymer molecules is given by

$$W=\left(1/\prod_{x=1}^{\infty}N_x!\right)\prod_{j=1}^{N}\nu_j, \quad (4)$$

where N_x is the number of polymer molecules composed of x units. Substituting Eq. (3) in (4) and simplifying the product term in the numerator,

$$W=\left[1\Big/\left(\sigma^N\prod_{x=1}^{\infty}N_x!\right)\right][(\gamma-1)/n_0]^{\sum_{j=1}^{N}(x_j-1)}$$
$$\times\left[n_0!\Big/\left(n_0-\sum_{i=1}^{N}x_i\right)!\right].$$

Noting that

$$\sum_{j=1}^{N}x_j=\sum_{i=1}^{N}x_i=\sum_{x=1}^{\infty}xN_x,$$

and replacing n_0 with

$$n_0=n+\sum_{x=1}^{\infty}xN_x$$

where n is the number of solvent molecules,

$$W=[1/(\sigma^N\prod N_x!)][(\gamma-1)/(n+\sum xN_x)]^{\sum(x-1)N_x}$$
$$\times[(n+\sum xN_x)!/n!]. \quad (5)$$

In Eq. (5) and in those which follow, the limits on the summations are omitted inasmuch as they invariably run from $x=1$ to ∞.

The entropy of mixing is given by $k \ln W$, where k is Boltzmann's constant. Or, if at this point n and the N_x's are expressed in moles, rather than as numbers of molecules,

$$\Delta S_{\text{mixing}}=R \ln W.$$

Substituting for W from Eq. (5) and introducing Stirling's approximation for factorial terms,

$$\Delta S_{\text{mixing}}=-R\left\{n \ln\left(\frac{n}{n+\sum xN_x}\right)\right.$$
$$+\sum\left[N_x \ln\left(\frac{N_x}{n+\sum xN_x}\right)\right]$$
$$\left.-\sum[(x-1)N_x][\ln(\gamma-1)-1]+N \ln \sigma\right\} \quad (6)$$

or

$$\Delta S_{\text{mixing}}=-R\{n \ln v_1+\sum[N_x \ln(v_x/x)]$$
$$-\sum[(x-1)N_x][\ln(\gamma-1)-1]+N \ln \sigma\}, \quad (6')$$

where v_1 and v_x are volume fractions of solvent and x-mer, respectively. In writing these equations the term for solvent (first term) could have been included with the first summation, the solvent being considered as a "polymer" composed of one segment. However, in consideration of possible heats of interaction between solvent molecules on the one hand and polymer segments on the other, it will facilitate formulation of free energy expressions to keep these terms separate.

In deriving Eqs. (6) and (6′) the liquid structure has been approximated by a lattice composed of cells equal in size to one solvent molecule. This physical approximation has received due consideration in previous publications. In the case of heterogeneous polymers, however, it leads to a summation term[12] $\sum N_x \ln(v_x/x)$ which contains only integral values of x. In applying these and subsequent

[12] The other summation terms in Eqs. (6) and (6′) represent merely total number of segments and of molecules.

equations to actual heterogeneous polymers it will be necessary to let this summation include the actual molecular species, for which x, the ratio of the molecular volumes of polymer molecule and solvent, will in general be non-integral. The additional approximation introduced by this extension will be negligible so long as the x values concerned are large. It should be borne in mind, however, that in subsequent equations the x values may not necessarily be integral.

The above expressions (6) and (6′) refer to the entropy change on forming the solution from N_1, N_2, N_3, etc. molecules of monomer, dimer, trimer, etc., each initially in an ordered (crystalline) state, and n molecules of solvent. This entropy change can be separated into three components: (*a*) the entropy of disorientation of the individual pure components, (*b*) the entropy of mixing these, and (*c*) the entropy of dilution of the mixture.

$$\Delta S_{\text{mixing}}=\Delta S_a+\Delta S_b+\Delta S_c. \tag{7}$$

The quantity ΔS_a is, of course, the sum of the entropies of disorientation of the individual polymer species.[6] For the x-mer species

$$\Delta S_{a,x}=RN_x[\ln(x/\sigma)+(x-1)\ln(\gamma-1)-(x-1)].$$

Hence,

$$\Delta S_a=R\sum[N_x\ln(x/\sigma)]+R\sum[(x-1)N_x][\ln(\gamma-1)-1]. \tag{8}$$

Subtracting this entropy of disorientation from Eq. (6) and setting $n=0$,

$$\Delta S_b=-R\sum[N_x\ln(xN_x/\sum xN_x)]. \tag{9}$$

This equation represents the entropy of mixing together the previously disoriented individual polymer species.

Finally, for the entropy change on diluting the mixed, disoriented polymer molecules with n molecules of solvent

$$\Delta S_c=\Delta S_{\text{mixing}}-\Delta S_a-\Delta S_b$$

$$=-R\left\{n\ln\left(\frac{n}{n+\sum xN_x}\right)+\sum\left[N_x\ln\left(\frac{\sum xN_x}{n+\sum xN_x}\right)\right]\right\} \tag{10}$$

$$=-R(n\ln v_1+N\ln v_2), \tag{10′}$$

where v_2 is the volume fraction of all polymer molecules; i.e.,

$$v_2=\sum v_x.$$

Equation (10′) is identical with the equation previously derived[6] for the entropy of mixing N disoriented polymer molecules, all of the same size, with n solvent molecules. When dealing with situations in which no change in the distribution of polymer species is encountered, this equation may be employed as the basic entropy of mixing expression without reservations for heterogeneity. In the expression previously derived[5,6] for partial molal quantities it is only necessary to replace the number of segments x with its number average $\bar{x}_n$. In short, heterogeneity can be disregarded, provided that the polymer is confined to one phase and that no polymerization and/or degradative steps are involved within that phase. For example, vapor pressures and osmotic pressures of polymer-solvent mixtures can be handled using ΔS_c, as previously published,[5,6,9] without regard for heterogeneity of the polymer. It is necessary, however, that the number average molecular weight, rather than some other average, be employed.

When two phases containing polymer are in equilibrium, passage of polymer from one phase to another being permissible, the undiluted, heterogeneous mixture of polymer molecules of given distribution is no longer adequate as a reference state. For the treatment of certain problems, e.g., chemical equilibria between polymer species (i.e., condensation or addition reactions between polymer species, or equilibrium degradation of the polymer molecules), Eqs. (6) or (6′) should be employed as the basic entropy of mixing expressions. The state in which the individual species are separate and oriented then represents the standard reference state.

In other cases it may be more convenient to employ the unmixed, disoriented species for the reference state. This reference state is sufficient for the treatment of the equilibria encountered in the fractionation of high polymers by fractional precipitation or solution. The entropy of mixing the separate, disoriented species with

solvent is given by

$$\Delta S^*_{\text{mixing}} = \Delta S_b + \Delta S_c$$

$$= -R\left\{n \ln \left(\frac{n}{n+\sum xN_x}\right) + \sum\left[N_x \ln \left(\frac{xN_x}{n+\sum xN_x}\right)\right]\right\} \quad (11)$$

$$= -R[n \ln v_1 + \sum(N_x \ln v_x)]. \quad (11')$$

An equation of this form for the entropy of mixing in a heterogeneous polymer solution was predicted by Gee[13] as an empirical extension of the entropy of mixing expression[6] for a solution composed of a single polymer component.

PARTIAL MOLAL ENTROPIES

As has been pointed out above, depending on the application, any one of three standard reference states—the disoriented mixture of polymer species in the absence of solvent; the disoriented, separated polymer species; or the oriented pure components—may be preferable. If the first-mentioned reference state is to be employed (ΔS_c) the partial molal functions previously derived,[5,6] wherein x is replaced by $\bar{x}_n$, will suffice. For the other two cases either ΔS^* of Eq. (11) or ΔS of Eq. (6) must be differentiated to obtain the partial molal entropies. These are given below.

For the partial molal entropy of the solvent per mole,

$$\Delta\bar{S}_1 = \partial\Delta S/\partial n = \Delta\bar{S}_1^* = \partial\Delta S^*/\partial n$$

$$= -R\left[\ln\left(\frac{n}{n+\sum xN_x}\right)+1 - \frac{n}{n+\sum xN_x} - \frac{\sum N_x}{n+\sum xN_x}\right]$$

$$= -R[\ln(1-v_2)+v_2-\sum(v_x/x)].$$

Or, since the number average molecular size $\bar{x}_n$ is given by

$$\bar{x}_n = \sum xN_x/\sum N_x = v_2/\sum(v_x/x)$$

$$\Delta\bar{S}_1 = \Delta\bar{S}_1^* = -R[\ln(1-v_2)+v_2(1-1/\bar{x}_n)], \quad (12)$$

which is identical with the expression previously derived,[5,6] except that x has been replaced by $\bar{x}_n$.

For the polymer constituents

$$\Delta\bar{S}_x = \partial\Delta S/\partial N_x$$

$$= -R\left\{\ln\left(\frac{N_x}{n+\sum xN_x}\right)+1 - \frac{xn}{n+\sum xN_x} - \frac{x\sum N_x}{n+\sum xN_x} - (x-1)[\ln(\gamma-1)-1]+\ln\sigma\right\}$$

$$= -R[\ln(v_x/x)+v_2x(1-1/\bar{x}_n) - (x-1)\ln(\gamma-1)+\ln\sigma]. \quad (13)$$

Similarly

$$\Delta\bar{S}_x^* = -R[\ln v_x-(x-1)+v_2x(1-1/\bar{x}_n)]. \quad (14)$$

PARTIAL MOLAL FREE ENERGIES

Assuming that the heat of mixing of solvents with polymer can be expressed in the van Laar form, then

$$\Delta H = B(V_1 n)\sum V_x N_x/(V_1 n+\sum V_x N_x),$$

where V_1 is the molar volume of solvent, V_x is the molar volume of the x-mer polymer species, B is a constant characteristic for each solvent-polymer pair, and the summations are over all polymer species. This can be written

$$\Delta H = BV_1 n\sum xN_x/(n+\sum xN_x) \quad (15)$$

since $V_x = xV_1$.

The partial molal heats of mixing are obtained by differentiation.

$$\Delta\bar{H}_1 = \partial\Delta H/\partial n = BV_1 v_2^2, \quad (16a)$$

$$\Delta\bar{H}_x = \partial\Delta H/\partial N_x = BxV_1 v_1^2. \quad (16b)$$

Combining these experiments with those given above for the partial molal entropies,

$$\Delta\bar{F}_1 = \Delta\bar{F}_1^* = \Delta\bar{H}_1 - T\Delta\bar{S}_1$$

$$= RT[\ln(1-v_2)+v_2(1-1/\bar{x}_n)+\mu v_2^2], \quad (17)$$

where $\mu = BV_1/RT$. Similarly,

$$\Delta\bar{F}_x = RT[\ln(v_x/x)+v_2x(1-1/\bar{x}_n) - (x-1)\ln(\gamma-1)+\ln\sigma+\mu x(1-v_2)^2] \quad (18)$$

[13] G. Gee, Rubber Chem. Tech. 17, 672 (1944).

and

$$\Delta\bar{F}_x^* = RT[\ln v_x - (x-1) + v_2 x(1-1/\bar{x}_n) + \mu x(1-v_2)^2]. \quad (19)$$

Huggins[5,9] has shown that the data available on solvent activities in solvent-polymer mixtures agree very well with Eq. (17) when μ is suitably chosen.[14a] In accordance with theory, μ is found to be characteristic for a given solvent-polymer pair at a given temperature, quite independent of concentration. Huggins has tabulated μ values for various systems.

Only in one case have solvent activities been measured carefully over the entire concentration range, namely, the benzene-rubber system thoroughly investigated by Gee and Treloar.[10] Huggins has shown that a single value of μ suffices to establish a good correlation between Eq. (17) and observed activities at all concentrations. Gee and Treloar also measured activities of the benzene-rubber system at different temperatures, thus enabling the separate evaluation of the partial molal entropy and partial molal heat of dilution. In dilute solutions the partial molal entropy is not in accord with Eq. (12), nor is the partial molal heat of dilution consistent with Eq. (16a) throughout the concentration range.[8,10,13] The former quantity approaches the theory as the concentration of rubber is increased. When these two somewhat erroneous equations are combined, however, a satisfactory free energy function is obtained, as Huggins has shown.

The basis for this divergence between the present theory of polymer solutions and experimental entropies has become evident from further theoretical research into the nature of dilute polymer solutions.[8] It is unnecessary to go into the causes for the discrepancies further than to point out that in the theory as here (and previously) developed it is assumed, with reference to the jth molecule to be added to the lattice, that all previously added molecules present a perfectly random distribution of cells occupied by polymer chain segments. This is not a satisfactory approximation in dilute solutions of high polymers. Here the occupied sites are present in loose "clusters," each polymer molecule occupying a "cluster" of consecutively adjacent cells. Intervening regions between these "clusters" are completely vacant.

For present purposes it is sufficient to point out that the theory, as given in previous papers and as extended here, yields an expression for the partial molal entropy which when combined with the μ term gives a partial molal free energy of the solvent which agrees well with experiment. It is only necessary to modify the significance of μ to include, in addition to the heat term, contributions from other factors the origins of which are not yet clear.[14b] With μ redefined in this way, Eq. (17) appears to depict the partial molal free energy of the solvent satisfactorily.

For the two-component system consisting of a single polymer species of size x dissolved in a solvent, the condition

$$(\partial\Delta\bar{F}_x/\partial n) = (\partial\Delta\bar{F}_1/\partial N_x)$$

or

$$(\partial\Delta\bar{F}_x/\partial v_1) = (xv_1/v_x)(\partial\Delta\bar{F}_1/\partial v_x)$$

necessarily applies. This connection permits derivation of the concentration dependent terms of $\Delta\bar{F}_x$ from $\Delta\bar{F}_1$. Thus, since Eq. (17) accounts satisfactorily for experimentally observed partial molal free energies of the solvent in two component systems composed of polymer and solvent (in which case $v_x = v_2$ and $\bar{x}_n = x$), then it necessarily follows that

$$\Delta\bar{F}_x = RT[\ln v_x + v_x x(1-1/x) + \mu x(1-v_x)^2 + \text{const.}] \quad (18')$$

must be equally acceptable for the solute. Furthermore, Eq. (17) applies with approximately the same value of μ to all polymers of a given series regardless of molecular weight. Hence, Eq. (18′) must also be applicable to polymers of different molecular weights.

These, then, are the experimental facts justifying the use of Eq. (17) and, for solutions of one polymer component, Eq. (18′) as well. Returning to the theory, it will be recalled that

[14a] The parameter μ in this paper corresponds to Huggins' μ_1.

[14b] Huggins' treatment, which differs slightly from that of the writer, leads to a theoretically derived μ which includes other terms in addition to the heat term. However, in the opinion of the writer these are trivial in comparison with the difference between the value of μ required to reproduce the observed activities and the value of $\Delta\bar{H}_1/RT$ obtained from temperature coefficients.

no significant new assumptions are required in the generalization of the treatment to apply to heterogeneous polymers. It is justifiable, therefore, to place equal confidence in the expression

$$\Delta\bar{F}_x = RT[\ln v_x + v_2 x(1-1/\bar{x}_n) + \mu x(1-v_2)^2 + \text{const.}] \quad (18'')$$

for the partial molal free energy of x-mer in a solution of a heterogeneous polymer.

The terms of Eq. (18) which are replaced by an undetermined constant in Eq. (18'') originate from the entropy of disorientation. The limitations of the theory in accounting for entropies in dilute solution have nothing to do with the validity of these terms in the free energy function. This portion of the partial molal free energy expression (18) rests squarely upon the theory in its present state of development, and is neither supported nor contradicted by experimental results.

The above arguments have been presented rather in detail in an effort to show clearly the justification for usings Eqs. (17) and (18), or (19), to represent the partial molal *free energies*, even in dilute solutions where the present theory fails to give correct *entropies*. In the following sections these equations will be applied as semi-empirical approximations to the actual free energy functions.

APPLICATION TO THE FRACTIONATION OF HIGH POLYMERS

Frequently it is desirable to separate a high polymer into a series of fractions differing in average molecular weight. This is usually accomplished by fractional precipitation. Either of two methods may be employed: Fractions of successively decreasing molecular weights may be obtained by adding a precipitant in suitably controlled increments to a dilute solution of the polymer maintained at constant temperature, the precipitate formed after each addition of precipitant being separated from the supernatant solution; or a simple solvent medium is employed from which precipitation is induced by lowering the temperature in suitable stages. It is necessary, of course, to assure equilibration after each addition of precipitant, or after each decrease in temperature. In a few instances fractional solution rather than fractional precipitation has been employed.

In all of these methods, separation of successive fractions depends on a controlled alteration of μ in the critical region for precipitation. This critical region occurs when μ exceeds one-half.[6] Except in the case of polymers which precipitate in crystalline form, the precipitates so obtained are liquid phases containing large amounts of solvent, although the concentration of polymer therein exceeds considerably the concentration in the supernatant phase. Fractionation depends upon the partition of each polymer species between these two phases. Higher polymers preferentially occur in the more concentrated phase. It has been recognized that the resulting fractions are by no means sharp; each fraction contains a rather wide distribution of species, although it is less heterogeneous than the original polymer. The equations given above provide a means for calculating the degree of separation obtained in the fractionation of high polymers under various conditions. They may also be of assistance in clarifying the factors affecting the sharpness of separation.

As indicated above, it is assumed in the following analysis that no crystallinity, or related regular structure, occurs in the precipitated phase. Furthermore, all polymer species are assumed to possess the same composition and unit structure, their only differences residing in the lengths of their chains. This latter assumption assures that the same μ value applies to all species. It will be assumed further that μ possesses the same value in either phase. This last assumption in general will not be strictly true when the solvent medium comprises a mixture of solvent and precipitant. The two phases may contain different proportions of the precipitant. The magnitude of the differences in μ for the two phases which may arise from this source has not been investigated. However, introduction of different μ values for the two phases would not change the general nature of the results derived below. When a single liquid is used for the solvent medium and the fractions are obtained by successive decreases in temperature, this assumption becomes unnecessary.

For equilibrium between the two phases to exist it is necessary that the partial molal free

energy of each constituent be the same in both phases. Using primes to signify quantities referring to the precipitated phase, the conditions for equilibrium can be expressed as follows:

$$\Delta\bar{F}_1=\Delta\bar{F}_1', \quad \Delta\bar{F}_x=\Delta\bar{F}_x'.$$

Substituting from Eqs. (17) and (19), or (18),

$$\ln(1-v_2)+v_2(1-1/\bar{x}_n)+\mu v_2^2 = \ln(1-v_2')+v_2'(1-1/\bar{x}_n')+\mu v_2'^2, \quad (20)$$

$$(\ln v_x)/x+v_2(1-1/\bar{x}_n)+\mu(1-v_2)^2 = (\ln v_x')/x+v_2'(1-1/\bar{x}_n')+\mu(1-v_2')^2. \quad (21)$$

Equation (21) can be written

$$\ln(v_x'/v_x)=\alpha x, \quad (22)$$

where

$$\alpha=v_2(1-1/\bar{x}_n)-v_2'(1-1/\bar{x}_n')+\mu[(1-v_2)^2-(1-v_2')^2]. \quad (23)$$

The quantity α can be regarded as a partition factor. The ratio of concentrations of a given species in the two phases varies exponentially with x.

An equation equivalent to Eq. (22) has been obtained by Schulz.[15] In deriving his relationship Schulz assumed that partition between the two phases is governed solely by differences in heats of solution of polymer molecules in the two phases. He assumed that this difference should increase in proportion to the molecular weight; thus the larger molecules should be preferentially distributed in favor of the precipitated phase where their heat of mixing with the medium will necessarily be lower. He neglected entropy effects such as have been taken into account by the present theory. Nevertheless, Schulz's partition equation is equivalent to Eq. (22) above, and he has carried out significant calculations on the nature of the molecular weight distributions in fractionated polymers. The significance assigned by Schulz to the partition factor α must be revised, however. His definition of α in effect includes only the μ term of Eq. (23).

The application of Eq. (23) to fractionation problems can be indicated as follows. Let V and V' represent the volumes of the respective phases, and let Q_x and Q_x' represent the absolute volumes of x-mer in them; thus $Q_x=Vv_x$ and $Q_x'=V'v_x'$. Also, let Q_x^0 equal the total volume of x-mer, i.e., $Q_x^0=Q_x+Q_x'$, and let the ratio of volumes of precipitated and supernatant phases be represented by $r=V'/V$. Then according to Eq. (22),

$$Q_x=Q_x^0/(1+re^{\alpha x}), \quad (24)$$

$$Q_x'=re^{\alpha x}Q_x^0/(1+re^{\alpha x}). \quad (24')$$

Whereas the relative concentration of each species in the two phases is governed by α, their relative amounts depend also on r.

The conditions of fractionation depend jointly on α and r. Both the location of the mean molecular weight about which the polymer is divided between the two phases and the sharpness of the separation depend on the particular combination of these parameters. Let us characterize the location of the region of separation by the molecular weight, or x value, at which $Q_x=Q_x'$. Let this particular value of x be designated by x_a. Then according to Eqs. (24) and (24'),

$$\exp(\alpha x_a)=1/r.$$

Further, as an index of the efficiency of the separation let us consider the slope of the curve representing the proportion of x-mer in the precipitated phase plotted against x, at the point $x=x_a$. According to Eq. (24') this quantity is given by

$$[d(Q_x'/Q_x^0)/dx]_{x_a}=\alpha/4.$$

The relative efficiency ϵ can be defined as the increase in Q_x'/Q_x^0 per unit relative change in x when $x=x_a$

$$\epsilon=[d(Q_x'/Q_x^0)/d\ln x]_{x_a},$$

$$\epsilon=\alpha x_a/4=(1/4)\ln(1/r). \quad (25)$$

Thus the relative efficiency of separation increases as the log of the reciprocal of r, and is independent of the molecular weight region in which separation occurs.[15]

From Eq. (25) it is clear that the volume of the supernatant phase relative to the volume of the precipitated phase should be made as great as possible. The importance of this point gains further emphasis from the fact that, according to Eqs. (24) and (24'), the concentration of

[15] G. V. Schulz, Zeits. f. physik. Chemie **B46**, 137 (1940); *ibid.* **B47**, 155 (1940).

every species including the lowest is greater in the precipitated phase than in the more dilute phase, although for components well below the molecular weight region of separation these concentrations will be nearly equal. Efficient elimination of lower polymers from the precipitated phase is possible only in the presence of a very large supernatant phase. Consequently, the solution from which precipitation takes place should be very dilute.

From a consideration of the phase equilibrium diagram (Fig. 1) depicting the concentrations of the phases in equilibrium as a function of μ which in turn depends on temperature or amount of precipitant, it is obvious that the more dilute the solution the more concentrated will be the precipitated phase. Thus, dilution not only increases the volume of the supernatant phase, but it also produces a "deswelling" of the precipitated phase. Both of these changes contribute toward the desired decrease in r.

The phase equilibrium diagrams for high-polymer solutions are extremely unsymmetrical (Fig. 1). The critical concentration at which partial miscibility first develops with increasing μ occurs at a low concentration of polymer. This critical concentration for a homogeneous polymer is given[6] by

$$v_{2(\text{critical})} = 1/(1+\sqrt{x}).$$

It moves in the direction of more dilute solutions as the molecular weight (x) is increased. From an examination of the shift with molecular weight in the phase equilibrium curves shown in Fig. 1 for homogeneous polymers, it is clear that the greater the molecular weight, the greater the degree of swelling of the precipitated phase in equilibrium with a supernatant phase of given concentration. Therefore, with increase in the molecular weight at which precipitation occurs, it becomes increasingly important to use dilute solutions. In fact, if the concentration is not much less than v_2 (critical) as given above, very little fractionation is to be expected.

The above discussion indicates the nature of the dependence of fractionation characteristics on the parameters α and r. Unfortunately, these are not simple functions of externally controlled variables such as μ, which depends on the amount of precipitant or temperature. Equation (23) gives an indication of the complexity of the dependence of α on the concentrations of polymer in the two phases, on the number average molecular weights and on μ; the quantities other than μ on the right of Eq. (23) depend on the initial distribution and on the dilution. The following discussion is aimed at a simplification of these inter-relationships.

The ratio of the volumes of polymer (all species included) in the two phases, $\sum_x Q_x'/\sum_x Q_x$, must equal rv_2'/v_2, from which it follows that

$$\frac{\sum [Q_x^0 e^{\alpha x}/(1+re^{\alpha x})]}{\sum [Q_x^0/(1+re^{\alpha x})]} = \frac{v_2'}{v_2} \equiv \gamma, \qquad (26)$$

where the symbol γ has been introduced to represent this ratio. Equation (26) relates r, α, and the initial polymer distribution (the V_x^0's) on the one hand with the relative total polymer concentration v_2'/v_2 on the other.

The number average molecular weights are similarly related to these three quantities.

$$\bar{x}_n = \sum v_x/\sum (v_x/x) = v_2/\sum (v_x/x).$$

The quantity $v_2/\bar{x}_n$ which appears in the equation for α, and in subsequent equations is given by

$$v_2/\bar{x}_n = \sum (v_x/x) = (1/V) \sum [Q_x^0/x(1+re^{\alpha x})]. \qquad (27)$$

Similarly

$$v_2'/\bar{x}_n' = (1/V') \sum [(Q_x^0 re^{\alpha x})/x(1+re^{\alpha x})]. \qquad (28)$$

Replacing V' with rV and subtracting Eq. (27) from (28),

$$(v_2'/\bar{x}_n') - (v_2/\bar{x}_n) = (1/V) \sum [Q_x^0(e^{\alpha x}-1)/x(1+re^{\alpha x})].$$

It will be convenient to define a quantity δ as follows:

$$\delta = (1/v_2)[(v_2'/\bar{x}_n') - (v_2/\bar{x}_n)].$$

Since

$$V = \sum (Q_x/v_2) = (1/v_2) \sum [Q_x^0/(1+re^{\alpha x})],$$

it follows that δ is given by the following function of the initial distribution, r and α:

$$\delta = \frac{\sum [Q_x^0(e^{\alpha x}-1)/x(1+re^{\alpha x})]}{\sum [Q_x^0/(1+re^{\alpha x})]}. \qquad (29)$$

Returning now to Eq. (23) and solving for μ,

$$\mu=\frac{\alpha+(v_2'-v_2)-\delta v_2}{(v_2'-v_2)[2-(v_2'+v_2)]}. \quad (30)$$

Substituting this expression for μ into Eq. (20), which as yet has not been made use of, and rearranging,

$$[1-(v_2'+v_2)/2]\ln[(1-v_2)/(1-v_2')]$$
$$=(v_2'-v_2)+\alpha(v_2'+v_2)/2-\delta v_2.$$

Series expansion of the logarithmic term followed by combination of terms resulting from multiplication by the factor in brackets ultimately leads to

$$[(v_2'-v_2)^3/2]\left[\frac{1}{2\cdot3}+\frac{(2v_2'+2v_2)}{3\cdot4}+\frac{3v_2'^2+4v_2'v_2+3v_2^2}{4\cdot5}\cdots+\frac{(n+1)v_2'^n+2nv_2'^{n-1}v_2+\cdots(n+1)v_2^n}{(n+2)(n+3)}+\cdots\right]$$
$$=\alpha(v_2'+v_2)/2-\delta v_2. \quad (31)$$

The infinite series in braces is very nearly equal to $1/6(1-v_2'-v_2)$ so long as v_2 and v_2' are small. Making this substitution in Eq. (31),

$$(v_2'-v_2)^3/12(1-v_2'-v_2)=\alpha(v_2'+v_2)/2-\delta v_2. \quad (32)$$

The percentage error introduced by the approximation will be of the order of $(v_2'^2/10)100$, since $v_2<v_2'$. Letting the ratio of the polymer concentrations in the two phases be represented by $\gamma=v_2'/v_2$, Eq. (32) may be expressed alternatively as

$$(\gamma-1)^3v_2^2=12[1-v_2(\gamma+1)]\times[(\gamma+1)\alpha/2-\delta]. \quad (32')$$

The external variables associated with separation of heterogeneous polymers by fractional precipitation are the initial polymer distribution, the value of μ (determined by temperature and amount of precipitant), and the average polymer concentration, or concentration of polymer prior to separation into two phases. This average concentration is given by $(v_2+rv_2')/(1+r)$. The complexity of the relationships derived above is such that it has not been possible to deduce α and r directly from these independent variables. However, it is possible to obtain solutions by assigning arbitrary values to the dependent variables r and α and then solving for the physically independent variables. Given the initial distribution (the V_x^0's) and assumed values of r and α, $v_2'/v_2=\gamma$ can be obtained by executing the summations of Eq. (26). Similarly, δ may be obtained from Eq. (29). Substituting these values of γ and δ into Eq. (32'), the resulting quadratic equation can be solved for v_2. The value of v_2' is given by γv_2. The average concentration can then be deduced, and μ can be computed from Eq. (30). This completes the deduction of the independent variables from the assumed values of r and α. Since the polymer distribution in each phase is governed, according to Eqs. (24) and

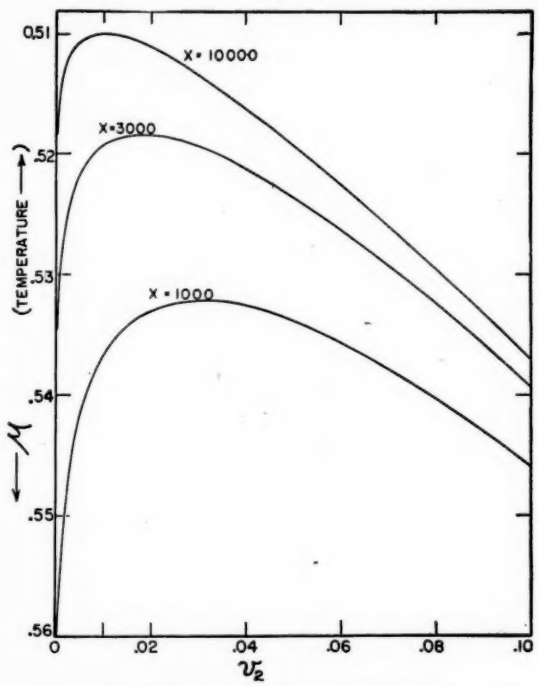


FIG. 1. Equilibrium phase compositions for solvent: homogeneous polymer mixtures in the region of partial miscibility for several values of x (relative molecular weight). Curves calculated from Eqs. (33) and (30). The pair of solutions for a given value of μ represent the calculated compositions of the phases in equilibrium. Since μ increases with decrease in temperature, the ordinate may be regarded as a temperature scale, and the curves should resemble temperature-composition diagrams for the binary liquid system.

(25), by r and α and the initial distribution, the solution for this particular set of independent variables, the V_x^0's, μ, and the average concentration, is complete.

Equation (32), or (32′), is useful also in deriving phase equilibria for homogeneous polymer-solvent systems. When only one polymer species composed of x segments is present, $v_2=v_x$ and $v_2'=v_x'$. Hence

$$\alpha=(\ln\gamma)/x, \quad \delta=(\gamma-1)/x$$

and Eq. (32′) reduces to

$$(\gamma-1)^3v_2^2=12[1-v_2(\gamma+1)] \times[(\gamma+1)(\ln\gamma)/2-(\gamma-1)]/x. \quad (33)$$

For any given value of x, this equation may be employed to obtain the concentrations of the two phases which are in equilibrium with one another. By substituting an arbitrary value for the ratio γ of these concentrations, solution of the quadratic equation (33) gives the concentration v_2 of the more dilute phase. Multiplication of v_2 by γ gives, of course, the concentration in the more concentrated phase. The corresponding value of μ can be found from Eq. (30). This procedure, based on the approximate equation (33), which is a modification of (32), is very much simpler than the method of successive approximations previously employed.[6]

Solutions of Eq. (33) are shown in Fig. 1 plotted against μ, for several values of x. The ordinate scale is plotted in the direction of decreasing μ. Since μ decreases with increase in temperature, these plots should resemble temperature-composition diagrams for the binary liquid systems. The positive direction of the ordinate axis corresponds to an increase in temperature, or to a decrease in the proportion of precipitant at constant temperature.

CHEMICAL EQUILIBRIA IN POLYMERIC SYSTEMS

An appropriate formulation of an equilibrium constant for a chemical reaction involving polymer formation, condensation, or degradation can be secured with certainty only when the dependences of the partial molal free energies (or the activities) of the reacting components on their concentrations are known. This is obvious from reference to the thermodynamic origins of the equilibrium constant. In this section the application of the above thermodynamic functions to the equilibria governing associative and degradative reactions of polymer molecules will be discussed.

Various condensation polymers which may be formed and degraded reversibly serve to illustrate the type of equilibria considered here. Polyesters, for example, are synthesized from their monomers by the reversible esterification reaction

$$x\text{HO—R—COOH}\rightleftarrows\text{HO[—R—COO—]}_x\text{H} +(x-1)\text{H}_2\text{O}.$$

The polymer molecules actually are not formed kinetically by the simultaneous condensation of x monomers; they are formed in an irregular stepwise succession of condensations, each of which is reversible,[16,17]

$$\text{HO[—RCOO]}_x\text{—H}+\text{HO[—RCOO—]}_y\text{H}\rightleftarrows \text{HO[—RCOO]}_{x+y}\text{—H}+\text{H}_2\text{O}.$$

Reactions of this character can be represented by the scheme[18]

$$A\text{—}B\rightleftarrows A\text{—}BA\text{—}BA\text{—etc.},$$

where A and B are the functional groups which co-react to form the inter-unit linkage AB. In this process a molecule such as water may or may not be split out. The following treatment is also applicable, with minor modifications to the polymerization of a pair of bifunctional monomers A—A and B—B, where the complementary functional groups reside in different monomers. Vinyl type polymerizations could be included, although these processes generally are not reversible in the thermodynamic sense.

As the standard reference state for each molecular species, a perfectly ordered hypothetical crystal will be chosen in which the molecules are arranged in perfect order. The standard states for the various species will possess similar structures insofar as the arrangement and packing of the units are concerned.

[16] P. J. Flory, J. Am. Chem. Soc. **61**, 3334 (1939).
[17] P. J. Flory, J. Am. Chem. Soc. **64**, 2205 (1942).
[18] P. J. Flory, J. Am. Chem. Soc. **58**, 1877 (1936).

Furthermore, the packing density will be so chosen that the heat change in passing to the actual liquid state with randomly arranged molecules is zero. It should be remarked that these conditions are introduced as definitions of an arbitrary standard state, and not as assumptions.

We now assume that with the standard states so defined the standard free energy change in a reaction

$$x\text{-mer}+y\text{-mer}\rightleftarrows(x+y)\text{-mer} \qquad (34)$$

is always the same regardless of x and y, and equal to ΔF^0. In other words, it is assumed that the standard free energy change for a reaction leading to the formation of one AB linkage (e.g., one ester group) is invariably equal to ΔF^0. This assumption can be expected to apply at all values of x and y when the functional groups A and B are separated sufficiently in the monomers so that the reactivity of A is influenced negligibly by previous reaction of the B group of the same unit, and vice versa. Furthermore, the intermolecular attractions of the A and B groups should not differ too much from that of the AB linking group. Even when these conditions are not met, the above assumption can be expected to apply satisfactorily except for low values of x and y.

The free energy of an x-mer admixed with other species, and possibly with a solvent as well, is given by

$$F_x=F_x^0+\Delta\bar{F}_x,$$

where F_x^0 is its free energy in the standard state and $\Delta\bar{F}_x$ is the free energy change in transporting one mole of x-mer from the standard state to an infinite amount of the mixture, or solution. In other words, $\Delta\bar{F}_x$ is the partial molal free energy of the x-mer in the mixture with respect to the standard state, as given by Eq. (18). According to the definition of the standard states and the assumptions introduced above,

$$F_x^0=xF_1^0+(x-1)\Delta F^0, \qquad (35)$$

where F_1^0 is the free energy of the monomer in the standard state and ΔF^0, as previously defined, is the standard free energy change per mole of inter-unit linkages AB in the molecule. The standard states have been defined with the purpose of view of obtaining an equation of the form of Eq. (35) wherein ΔF^0 is a constant. Hence,

$$F_x=x(F_1^0+\Delta F^0)-\Delta F^0+\Delta\bar{F}_x.$$

The total free energy of the mixture exclusive of inert solvent is given by

$$F=\sum N_xF_x=(F_1^0+\Delta F^0)\sum xN_x - \Delta F^0\sum N_x+\sum\Delta\bar{F}_xN_x. \qquad (36)$$

When the polymerization (or degradation) reactions have reached a state of equilibrium, $dF=0$. Taking the differential of Eq. (36) and equating to zero,

$$\sum(\Delta\bar{F}_x-\Delta F^0)dN_x=0, \qquad (37)$$

since constancy of the total amount of material requires that

$$\sum xdN_x=0, \qquad (38)$$

and since $\sum N_xd(\Delta\bar{F}_x)=0$, according to the Gibbs-Duhem equation. Equation (37) expresses the necessary condition for equilibrium.

If the process concerned is a simple one such as is expressed by Eq. (34), where only three species are involved, then

$$dN_x=dN_y=-dN_{x+y},$$

and for the equilibrium condition we have, according to Eq. (37),

$$\Delta\bar{F}_{x+y}-\Delta\bar{F}_x-\Delta\bar{F}_y+\Delta F^0=0.$$

After substituting from Eq. (18) for these partial molal free energies there is obtained

$$\ln K=-\Delta F^0/RT+\ln[(\gamma-1)\sigma], \qquad (39)$$

where

$$K=\left(\frac{v_{x+y}}{v_xv_y}\right)\left(\frac{xy}{x+y}\right). \qquad (40)$$

Alternatively

$$\ln K'=-\Delta F^0/RT+\ln[(\gamma-1)\sigma V_1], \qquad (39')$$

where V_1 is the molar volume per structural unit A—B, and

$$K'=c_{x+y}/c_xc_y, \qquad (40')$$

the c's representing the respective concentrations in moles per unit volume. Inasmuch as γ

is a function of the liquid structure only and σ and V_1 are constants characteristic of the types of molecules concerned, evidently either K or K' should be an acceptable equilibrium constant.

It should be noted that use of mole fractions instead of molar concentrations in expressing the equilibrium constant (except, of course, when the equilibrium constant is dimensionless) is irreconcilable with the statistical mechanics of these mixtures.[19] In the absence of diluent, conversion to mole fractions X_x through the substitutions

$$v_x = X_x \sum N_x / \sum xN_x,$$

etc., in Eq. (40) yields

$$[X_{x+y}/X_xX_y] = K \sum N_x / \sum xN_x = K \sum N_x / N_0,$$

where the total number of polymer segments, $\sum xN_x$, is replaced by N_0. Since $\sum N_x$ varies with the degree of displacement of the reaction, the quantity in brackets should not be employed as an equilibrium constant.

Proceeding now to the more complex equilibrium between all possible species M_x, or $(A—B)_x$, where all values of x are considered, we will again employ the equilibrium condition as expressed by Eq. (37). According to Eqs. (18) and (38),

$$\sum \Delta\bar{F}_x dN_x = RT \sum \{\ln (N_x v_2/N_0) + \ln [(\gamma-1)\sigma]\} dN_x. \quad (41)$$

Substituting Eq. (41) in (37)

$$\sum \left\{ \ln (N_x v_2/N_0) + \ln [(\gamma-1)\sigma] - \frac{\Delta F^0}{RT} \right\} dN_x = 0. \quad (42)$$

Solving Eqs. (38) and (42) by the Lagrange multiplier method,

$$N_x = (N_0/v_2) e^{-\beta} e^{-\lambda x}, \quad (43)$$

where λ is the multiplier and

$$\beta = \ln [(\gamma-1)\alpha] - \Delta F^0/RT.$$

It is found upon substituting Eq. (43) into the equation $\sum xN_x = N_0$, and carrying out the summation over integral values of x from 2 to ∞, that

$$e^{\beta} = e^{-\lambda}/v_2(1-e^{-\lambda})^2. \quad (44)$$

Also, the total number of molecules $\sum N_x$ must equal $N_0(1-p)$, where p is the "extent of reaction," or fraction of the initial A, or B, groups converted to AB. According to Eq. (43), after substituting Eq. (44) for e^{β},

$$\sum N_x = N_0(1-e^{-\lambda}).$$

Hence, $e^{-\lambda}$ may be identified with the extent of reaction p. Making this substitution and introducing Eq. (44) in (43),

$$N_x = N_0(1-p)^2 p^{x-1}, \quad (45)$$

which is the equation, previously derived[17,18] by other methods, for the molecular size distribution in linear condensation polymers.

Tobolsky[20] has derived the above molecular size distribution equation by a similar procedure based on the same thermodynamic equations.[6] He sought to introduce the effect of heat of polymerization into the equations, with particular reference to vinyl type polymerizations which invariably are exothermic. In so doing he erroneously employed the heat of reaction where a standard state free energy change obviously should be used. Consequently, an equilibrium constant derived from his treatment would depend on the former, rather than on the latter. The error can be corrected by substituting ΔF^0 for P (heat of reaction) in Tobolsky's equations. If pursued further, his treatment corrected in this manner would lead to conclusions equivalent to those reached here.

According to Eq. (44),

$$\beta = \ln [\sigma(\gamma-1)] - \Delta F^0/RT = \ln K, \quad (46)$$

where

$$K = p/v_2(1-p)^2. \quad (47)$$

Or

$$\ln K' = \ln [\sigma(\gamma-1)V_1] - \Delta F^0/RT, \quad (46')$$

where

$$K' = pV_1/v_2(1-p)^2 = c_{AB}/c_Ac_B. \quad (47')$$

c_{AB}, c_A, and c_B represent the concentrations of the respective functional groups in moles per unit

[19] R. E. Powell and H. Eyring, J. Am. Chem. Soc. **65**, 648 (1943), in their analysis of the equilibria in liquid sulfur between ring (S_8) and chain forms have expressed equilibrium constants in terms of mole fractions. According to the present treatment their equilibrium "constants" are not to be regarded as constants.

[20] A. V. Tobolsky, J. Chem. Phys. **12**, 402 (1944).

volume. Thus, polyfunctional condensations may be treated as reactions between functional groups without regard for the particular molecular species involved, a point of view set forth in previous publications.[16–18] The entropies of mixing of long chain polymers are such as to require no revision in this postulate as applied to chemical equilibria between polymeric reactants.[20]

It can be shown further that even the magnitude of the equilibrium constant should not be altered by the polymeric nature *per se* of the components in such equilibria. That is to say, the percentage esterification of a glycoldibasic acid mixture at equilibrium should be about the same as is found between analogous mono alcohols and carboxylic acids under equivalent conditions of temperature and dilution. A monofunctional reaction of this type comes within the scope of the treatment of the reaction (34). If there are initially c_0 moles of each of the two reactants per unit volume, then

$$c_A = c_B = c_0(1-p), \quad c_{AB} = c_0 p$$

and

$$c_0 = v_2/(V_A + V_B),$$

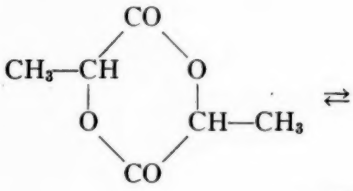
where V_A and V_B are the molar volumes of the reactants. Substituting in Eq. (40′)

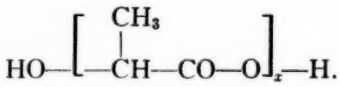
$$K' = p/(1-p)^2 c_0 = p(V_A + V_B)/v_2(1-p)^2,$$

which is identical with Eq. (47′) for the bifunctional reaction, except for the obvious replacement of V_1 by $(V_A + V_B)$.

In the above discussion the role of a by-product of the polymerization reaction, such as the water formed during polyesterification, has been disregarded. It is obvious from the above discussion, however, that equilibrium constants for condensation processes from which a by-product is released may be written in an analogous manner, the concentration of the by-product appearing in the numerator.

These generalizations concerning equilibria in polymer reactions can be applied to the frequently encountered reversible ring-chain equilibria. For example, the six-membered lactide ring[21] can be reversibly converted to a linear polyester





In this system two equilibria are to be considered: the ring-chain equilibria indicated above, and the polyesterification equilibrium, involving water as a by-product, which determines the average length of the chains. These chains will possess the size distribution given above, and this phase of the equilibrium may be treated as a reaction between functional groups. Other examples include numerous six-membered lactone rings which can be reversibly converted to chain polymers, the $(PNCl_2)_3 \rightleftarrows (PNCl_2)_x$ reaction,[22] aldehyde polymers, cyclic lactams, and the ring-chain sulfur transformation already referred to.[19]

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[21] W. H. Carothers, G. L. Dorough, and F. J. van Natta, J. Am. Chem. Soc. **54**, 761 (1932).

[22] See K. H. Meyer, reference 4, p. 52.

The Dielectric Properties of β-Lactoglobulin in Aqueous Glycine Solutions and in the Liquid Crystalline State

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(Received July 17, 1944)

The dielectric constant ϵ' and loss factor ϵ'' of solutions of β-lactoglobulin dissolved in aqueous 0.48, 1.5, and 2.5 molar glycine, and the dielectric constant of β-lactoglobulin liquid crystals have been measured for frequencies between 0.01 and 5.0 megacycles. The data show a broader frequency range of dispersion and absorption and a smaller value of ϵ''_{max} than is predicted by the Debye theory for a system characterized by a single relaxation time. The disparity between the experimental data and the Debye theory increased with the concentration of lactoglobulin and was greater than expected on the basis of the small effects of protein concentration on other physical properties of β-lactoglobulin, e.g., sedimentation constant. Dielectric constants for "zero" and "infinite" frequencies have been obtained by the Cole circular-arc method of extrapolation. The frequency dependence of ϵ' and ϵ'' was found to be well represented by the empirical equation of Cole and Cole, $\epsilon'-i\epsilon''=\epsilon_\infty+(\epsilon_0-\epsilon_\infty)/[1+(i\omega\tau_0)^{1-\alpha}]$. In this equation ϵ_0 and ϵ_∞ are, respectively, the dielectric constants for zero and infinite frequencies, $\omega=2\pi$ times the frequency, τ_0 is a generalized relaxation time, and α is a constant, $0<\alpha<1$. For $\alpha=0$, the equation reduces to that of Debye for a system characterized by a single relaxation time. For the solutions of β-lactoglobulin α was found to range from 0.08 to 0.4, depending upon the lactoglobulin and glycine concentrations. The relaxation time varied from 7.5 to 25×10^{-8} sec. for a change in lactoglobulin concentration of 3.5 to 94.0 grams per liter. The dipole moment is estimated to be $790\pm26\times10^{-18}$ e.s.u.

INTRODUCTION

THE importance of electrical properties for the characterization of proteins and other macromolecules has been established by many experimental studies. Exploratory experiments directed toward the characterization, by dielectric constant measurements, of such molecules and their enzymic degradation products, have revealed effects at high protein concentrations not previously reported. In view of the importance of these effects for the interpretation of dielectric constants in terms of molecular size, shape, and charge distribution, they have been systematically investigated for the protein β-lactoglobulin. Extensive dielectric measurements of dilute solutions containing one percent or less of this protein have been reported by Ferry and Oncley.[1] In the present paper dielectric constant measurements are reported for aqueous solutions of 0.48, 1.5, and 2.5 molar glycine containing up to about 10 percent of lactoglobulin and for lactoglobulin liquid crystals containing about 33 percent protein.

EXPERIMENTAL

Materials Studied and Their Preparation

The β-lactoglobulin used in this investigation was prepared from cow's milk by the method described by Palmer.[2] The preparation was crystallized five times by dialysis. Stock solutions of lactoglobulin in glycine were prepared by

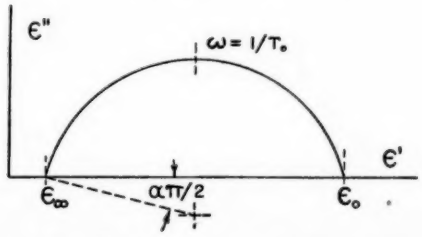

FIG. 1. Cole circle diagram for complex dielectric constant $\epsilon^*=\epsilon'-i\epsilon''$. The case illustrated is for $\alpha>0$. For $\alpha=0$ the center of the arc falls on the ϵ' axis. The maximum value of ϵ'' occurs for $\omega=1/\tau_0$.

* One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. The work reported was begun in 1939 in the Enzyme Laboratory of the Bureau and was completed in the Western Regional Research Laboratory.

[1] J. D. Ferry and J. L. Oncley, J. Am. Chem. Soc. **63**, 272 (1941).

[2] A. H. Palmer, J. Biol. Chem. **104**, 359 (1934).

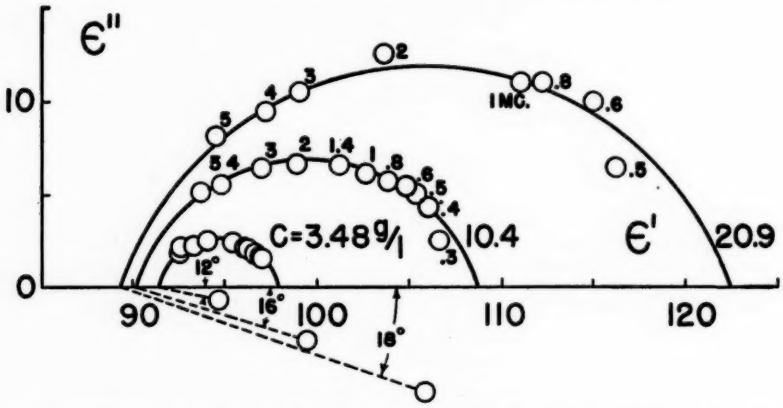

FIG. 2. Dielectric constant ϵ', and loss factor ϵ'', for solutions of β-lactoglobulin in 0.48 molar aqueous glycine at 20.0°C. Data are shown for lactoglobulin concentrations C equal to 3.48, 10.4, and 20.9 grams per liter.

adding crystals of lactoglobulin to glycine solutions. After analytical determination of the protein and glycine concentrations, the glycine concentration was adjusted to the desired value by the addition of solid glycine. To obtain solutions containing different amounts of lactoglobulin the stock solutions were diluted with glycine solutions containing the same amount of glycine as the stock solutions. In this way solutions containing various amounts of lactoglobulin dissolved in 0.48, 1.5, and 2.5 molar glycine were obtained. The concentrations of glycine and lactoglobulin were calculated from determinations of total nitrogen and protein nitrogen in the solutions. The *p*H of the solutions was between 5.6 and 6.0.

The liquid crystals* were prepared by dialyzing concentrated solutions of lactoglobulin containing sodium chloride until sufficient salt was removed to cause the protein to separate as a new phase. Excess water was removed from the protein phase by centrifugation and the liquid crystals were transferred to the dielectric cell. During the entire process of preparation, the temperature was maintained between 10° and 15°C.

Electrical Measurements

A detailed description of the apparatus and methods used to determine dielectric constants has been published previously.[3]

Briefly, dielectric constants and dielectric loss factors were obtained from substitution measurements of the capacitance and conductance of a micrometer-type cell containing the solution of lactoglobulin. Measurements were made for about twenty frequencies spaced more or less uniformly over the frequency range of 0.01 to 5.0 megacycles. The bridge equipment employed for these measurements is similar to that used by Oncley.[4] The test cell is a modified form of the electrolytic cells used by Fricke and Curtis[5] and by Cole and Curtis.[6]

In the capacitance measurements, lead inductance and electrode polarization were the principal sources of error and appropriate correction measures, already described in detail,[3] were taken. From calibration measurements in which glycine solutions of known dielectric constant were employed, the probable error in the dielectric constants was estimated to be ± 0.5 unit for the protein solutions and about ± 1.0 unit for the liquid crystals.

In the conductance measurements an empirical correction was made for the error introduced at the higher frequencies by lead inductance and skin effect in the wire-wound resistance standards. These corrections were obtained from a series of calibration measurements in which the dielectric test cell[3] filled with aqueous KCl solu-

* This material is the "oil" described by Palmer (reference 2).

[3] T. M. Shaw, J. Chem. Phys. **10**, 609 (1942).

[4] J. L. Oncley, J. Am. Chem. Soc. **60**, 1115 (1938).

[5] H. Fricke and H. J. Curtis, J. Phys. Chem. **41**, 729 (1937).

[6] K. S. Cole and H. J. Curtis, Rev. Sci. Inst. **8**, 333 (1937).

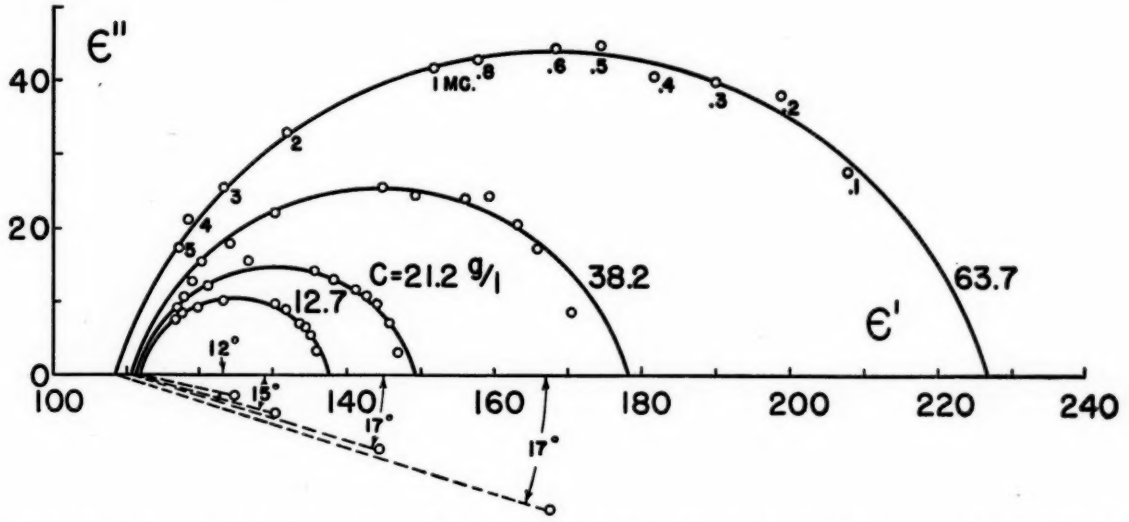

FIG. 3. Dielectric constant ϵ', and loss factor ϵ'', for solutions of β-lactoglobulin in 1.5 molar aqueous glycine at 20.0°C. Data are shown for lactoglobulin concentrations C equal to 12.7, 21.2, 38.2, and 63.7 grams per liter.

tions was used as a standard electrolytic resistor. The conductance of the electrolytic resistor was determined accurately at low frequencies by bridge measurements. It was assumed that the change in conductance of the electrolytic resistor over the frequency range of 0.01 to 5.0 Mc is negligible. Experimental tests[7] of the predictions of the Debye and Falkenhagen theory of electrolytic conductance indicate this assumption to be valid within the precision of the conductance measurements here reported. The over-all probable error in the conductance determinations was estimated to be ±0.5 percent.

For the purposes of the present work, the dielectric loss factor ϵ'' is defined by the equation,

$$\epsilon''=(G-G_0)d/K\omega, \qquad (1)$$

where G is the conductance at angular frequency ω, G_0 is the limiting conductance at low frequencies, K is a constant for the dielectric test cell equal to 0.1700 ± 0.0005 $\mu\mu$f cm, and d is the spacing of the test cell electrodes.

The use of Eq. (1) is based upon the assumption that the a.c. conductance of the dielectric approaches a constant limiting value G_0 at low frequencies removed from the frequency region of dielectric absorption. Values of G_0 were obtained in the present work from graphs of G *versus* log ω. The rate of change of G with frequency between 10^4 and 2×10^4 cycles, in all cases except for the liquid crystals, did not exceed the probable error in the conductance measurements (0.5 percent). It should be noted from Eq. (1) that even small errors in G_0 may lead to very large errors in ϵ'', particularly at the lower frequencies or for solutions where the total energy absorption is small and G is nearly equal to G_0.

RESULTS AND DISCUSSION

A convenient quantitative description of the dispersion and absorption of many dielectrics is afforded by the empirical equation recently described by Cole and Cole,[8]

$$(\epsilon^*-\epsilon_\infty)/(\epsilon_0-\epsilon_\infty)=[1+(i\omega\tau_0)^{1-\alpha}]^{-1}. \qquad (2)$$

In this equation ϵ^* is the complex dielectric constant equal to $\epsilon'-i\epsilon''$, where ϵ' is the ordinary dielectric constant, ϵ'' is the a.c. loss factor, ω is the angular frequency equal to 2π times the electrical frequency ν, ϵ_0 and ϵ_∞ are the limiting values of ϵ' for zero and infinite frequencies, respectively, τ_0 is a generalized relaxation time, and α is a parameter ranging from 0 to 1. For $\alpha=0$, Eq. (2) reduces to the equation given by Debye[9] for polar dielectrics.

[7] O. M. Arnold and J. W. Williams, J. Am. Chem. Soc. **58**, 2616 (1936).

[8] K. S. Cole and R. H. Cole, J. Chem. Phys. **9**, 341 (1941).

[9] P. Debye, *Polar Molecules* (Chemical Catalog Company, New York, 1929).

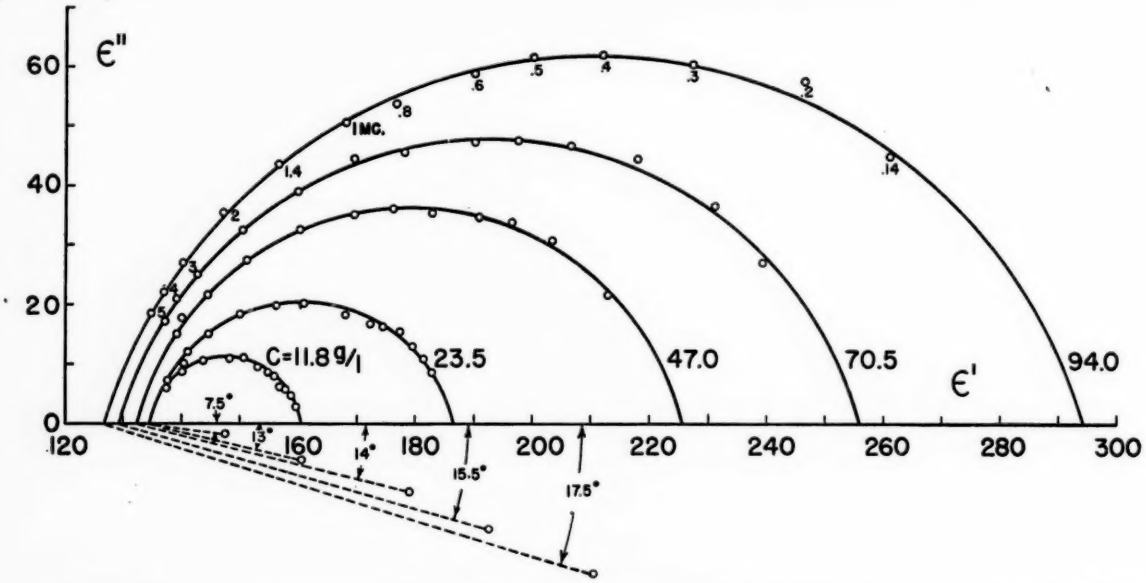

FIG. 4. Dielectric constant ϵ', and loss factor ϵ'', for solutions of β-lactoglobulin in 2.5 molar aqueous glycine at 20.0°C. Data are shown for lactoglobulin concentrations C equal to 11.8, 23.5, 47.0, 70.5, and 94.0 grams per liter.

The real and imaginary components of Eq. (2) are

$$(\epsilon'-\epsilon_\infty)/(\epsilon_0-\epsilon_\infty)=\tfrac{1}{2}\{1-\sinh(1-\alpha)x/[\cosh(1-\alpha)x+\sin(\alpha\pi/2)]\}, \quad (3)$$

and

$$\epsilon''/(\epsilon_0-\epsilon_\infty)=\tfrac{1}{2}\cos(\alpha\pi/2)/[\cosh(1-\alpha)x+\sin(\alpha\pi/2)], \quad (4)$$

where

$$x=\log_e(\omega\tau_0).$$

The principal advantage of Eq. (2) is that it provides a quantitative description of the *experimental* behavior of dielectrics. As is well known, the classical Debye equations[9] fail to provide, in many cases, more than a qualitative description of the behavior of the dielectric constant and loss factor.[8]

Experimental data which satisfy Eq. (2) yield a circular arc when ϵ'' is plotted against ϵ'. If a semicircle is obtained with center on the ϵ' axis then $\alpha=0$ and, as previously noted, Eq. (2) reduces to the Debye equation for a polar dielectric with a single relaxation time. If, however, an arc with center depressed below the ϵ' axis is obtained, then $\alpha>0$ and a distribution of relaxation times is indicated. This situation is illustrated in Fig. 1 where a graphical method of obtaining α is represented.

Plots of ϵ'' *versus* ϵ' for solutions of β-lactoglobulin in aqueous glycine are shown in Figs. 2–4. In all cases the data are well represented by circular arcs with centers depressed below the ϵ' axis. It is immediately apparent that the angle by which the center of the arc is depressed below the ϵ' axis varies with the composition of the solution. To investigate this dependence, values of α have been obtained for each of the circle diagrams in the manner outlined in Fig. 1. The resulting data are presented in Fig. 5 where α is plotted as a function of the concentrations of β-lactoglobulin and glycine. Figure 5 shows that for all protein concentrations studied $\alpha>0$ and hence the experimental data cannot be represented by the Debye equations which apply only to a system with a single relaxation time. Moreover, α increases with increasing protein concentration and with decreasing concentration of glycine in the solvent. The extent of the failure of the Debye equations to represent the experimental data becomes more apparent if use is made of Eqs. (3) and (4). In Figs. 6 and 7, typical dispersion and loss factor curves are shown for solutions of β-lactoglobulin representing extremes of concentration. The solid line curves were calculated from Eqs. (3) and (4) using the parameters ϵ_0, ϵ_∞, and α obtained from the circle diagrams of

Fig. 3.[10] The broken line curves marked $\alpha=0$ are the so-called Debye curves. The agreement between experimental data and the curves calculated from Eqs. (3) and (4) for $\alpha>0$ is good in all cases.

Dielectrics characterized by a distribution of relaxation times[11,12] yield circle diagrams with $\alpha>0$, similar to those shown in Figs. 2–4 for β-lactoglobulin solutions.

In all cases such systems can be characterized by a symmetrical distribution of relaxation times about a central or most probable relaxation time τ_0. The numerical value of τ_0 can be obtained from the experimental data in a number of ways. Cole and Cole suggest a graphical method based on Eq. (2).* Probably the most convenient method is that described by Fuoss and Kirkwood.[13] The relaxation time is calculated from the frequency ν_m for which $\cosh^{-1}(\epsilon''_{max}/\epsilon'')=0$ according to the relation $\tau_0=1/(2\pi\nu_m)$. In the present work the frequency ν_m was determined graphically. In the few instances where a comparison of the Cole method with that of Fuoss and Kirkwood was made, no significant differences in τ_0 were found.

The relaxation times obtained for the β-lactoglobulin solutions are shown in Fig. 8 where τ has been plotted as a function of the β-lactoglobulin concentration C. A correction for the solvent viscosity has been applied to τ_0 to reduce the relaxation times to a comparable basis. According to Debye the relaxation time varies with the viscosity and absolute temperature of the solvent. Accordingly the values of τ_0 have been corrected to correspond to the viscosity of water at 20°C by the equation,

$$\tau=\tau_0(\eta_w/\eta_s),$$

where τ is the relaxation time in water at 20°C, η_w = viscosity of water at 20°C, η_s = viscosity of solvent corresponding to the observed relaxation time τ_0.

The data in Fig. 8 show that τ increases with increasing concentration of β-lactoglobulin but is independent of the glycine concentration of the solvent. Evidently, the mechanism causing the increased relaxation time with increasing C is dependent only on the number of lactoglobulin molecules in the solution. The value of τ obtained by *extrapolation* to $C=0$ of the curve given in Fig. 8, is very close to $7.5\pm0.5\times10^{-8}$ sec., in agreement with the value obtained by Ferry and Oncley.[1]

It should be remarked that the absolute values given for the relaxation time in Fig. 8 are subject to considerable uncertainty due to the lack of an adequate theory for the local field in polar liquids. The results shown in Fig. 8 are based on the assumption that the Onsager[14] theory of the local

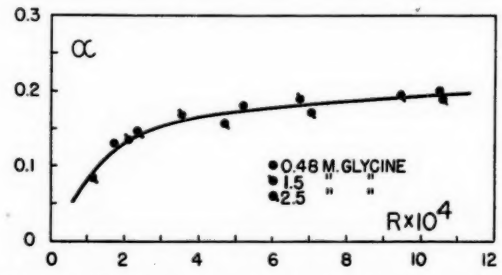

FIG. 5. Variation of α with mole fraction ratio R. (R equals mole fraction β-lactoglobulin divided by mole fraction of glycine.)

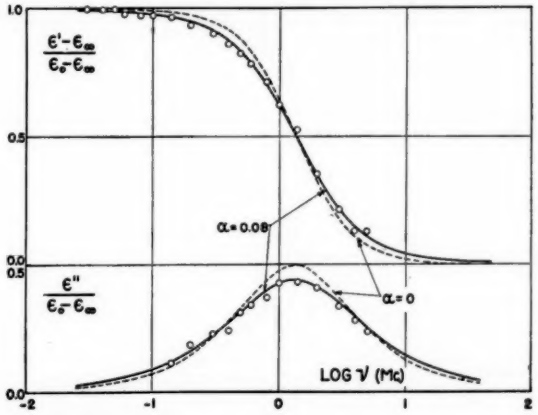

FIG. 6. Frequency variation of dielectric constant and loss factor, according to Eqs. (3) and (4), for solution containing 11.8 grams per liter of β-lactoglobulin dissolved in 2.5 molar aqueous glycine at 20.0°C.

[10] Since the fourth parameter τ_0 needed in the calculation could not be obtained precisely from the ϵ'' *versus* ϵ' plots, the required values were obtained from graphs of $\cosh^{-1}(\epsilon''_{max}/\epsilon'')$ *versus* $\log\nu$, according to a method of Fuoss and Kirkwood, described below.

[11] R. M. Fuoss, J. Am. Chem. Soc. **63**, 2401 (1941).

[12] It should perhaps be noted that the ϵ' and ϵ'' data of W. R. Conner, J. Chem. Phys. **9**, 591 (1941), for a polydisperse solution of maple lignin in chloroform when plotted according to the Cole method yield a circular arc with $\alpha=0.25$.

* See reference 8, Eq. (6).

[13] R. M. Fuoss and J. Kirkwood, J. Am. Chem. Soc. **63**, 385 (1941).

[14] L. Onsager, J. Am. Chem. Soc. **58**, 1486 (1936).

field is valid for the β-lactoglobulin solutions. If on the other hand, the Clausius-Mosotti value for the field were assumed valid, the values of τ would be reduced by a factor $(\epsilon_\infty+2)/(\epsilon_0+2)$.

The form of the dielectric dispersion is particularly important with reference to questions regarding the shape of the lactoglobulin molecule. Ferry and Oncley[1] studied the dispersion of lactoglobulin solutions containing up to 7.7 g/l at temperatures of 0° and 25°C. Over the concentration range studied by them, Ferry and Oncley found no significant differences in the form of the dispersion or in the magnitude of the relaxation time. Comparison of their experimental dispersion curves with curves calculated from the Debye theory for a single relaxation time (spherical molecule) and on the basis of two relaxation times for an spheroidal molecule showed reasonably good agreement of the 25° data with either of the theoretical curves. For the 0° data, however, the agreement was considered better in the case of the theoretical curve for the spheroidal model. Shack, studying the dielectric adsorption of β-lactoglobulin, obtained data indicating the existence of a single relaxation time.[15]

It has been shown above that the dispersion data obtained in the present investigation cannot be represented by the Debye theory for a single relaxation time. Moreover, it appears to be of doubtful significance to attempt an interpretation based on an assumed spheroidal or ellipsoidal molecule with two (or three) relaxation times. This follows from the fact that the form of the dispersion is not constant but depends markedly upon the lactoglobulin concentration (see Fig. 5), and if the observed dispersion is to be interpreted on the basis of more than one relaxation time then it would appear necessary to assume a broad and approximately continuous distribution of relaxation times. Otherwise as Cole and Cole[8] have indicated, the ϵ'' *versus* ϵ' locus (see Figs. 2–4) would be required to have 90° angles of approach to the ϵ' axis for zero and infinite frequencies.

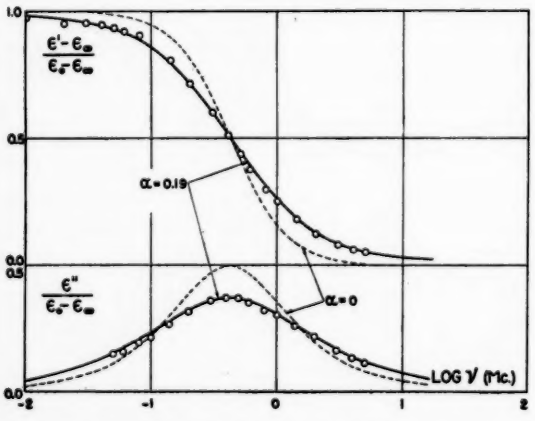

FIG. 7. Frequency variation of dielectric constant and loss factor, according to Eqs. (3) and (4), for solution containing 94.0 grams per liter of β-lactoglobulin dissolved in 2.5 molar aqueous glycine at 20.0°C.

Ferry and Oncley did not report values of ϵ''. Such values are tedious to calculate, in order to prepare a plot of ϵ'' *versus* ϵ' for their data. However, it has been shown by trial that Eq. (3) fits the data of Ferry and Oncley satisfactorily if α is chosen equal to 0.04 ± 0.01. It would appear impossible, therefore, on the basis of existing data for dilute solutions of lactoglobulin to distinguish between an interpretation based upon an assumption of two relaxation times (spheroidal model) and an interpretation involving some factor empirically described by α. However, for the more concentrated solutions, the assumption of a spheroidal or ellipsoidal molecule (two or three relaxation times) appears inadequate to explain the data. Whether β-lactoglobulin at infinite dilution should be represented by more than one relaxation time cannot be concluded from existing data.

On the other hand, for concentrations of lactoglobulin of the order of 1 percent or more it seems clear that there is involved a symmetrical distribution of relaxation times about a central or most probable value. On the assumption that this interpretation is correct the actual distributions can be calculated by the use of the distribution function given by Cole and Cole.*

There remains, however, the problem of accounting for the mechanism giving rise to the assumed distribution of relaxation times. Many possibilities have been suggested[16,17] but it is difficult in view of the present state of development of the theory of polar solutions to do more

[15] J. L. Oncley in Chapter 22 of E. J. Cohn and J. T. Edsall, *Proteins, Amino Acids, and Peptides* (Reinhold Publishing Corporation, New York, 1943).

* See reference 8, Eq. (13).

[16] W. A. Yager, Physics **7**, 434 (1936).

[17] W. Kauzmann, Rev. Mod. Phys. **14**, 12 (1942).

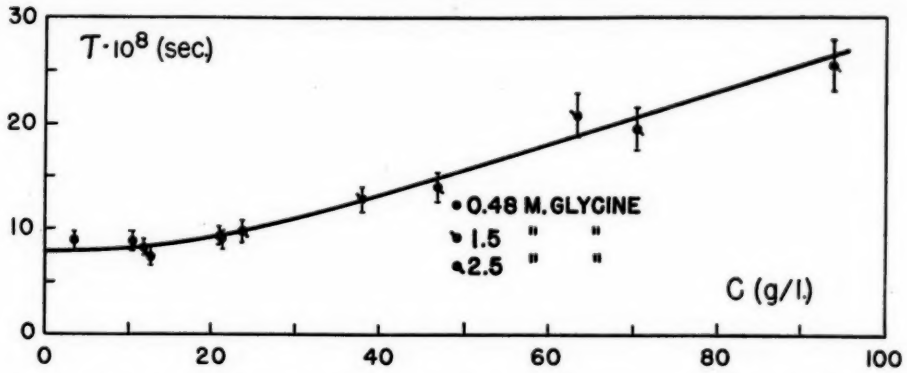

FIG. 8. Variation of relaxation time, $\tau=\tau_0(\eta_w/\eta_s)$, with concentration of β-lactoglobulin C. Data are shown for solvents containing 0.48, 1.5, and 2.5 moles glycine in water.

than acknowledge the reasonableness of such a behavior. It must certainly be agreed that a solution of highly polar protein molecules dissolved in a polar medium (aqueous glycine) offers many opportunities for interactions which undoubtedly would be reflected in the relaxation time. In fact, it would be notable if they were not. The data presented in Fig. 5 show clearly that in a solution containing a fixed concentration of glycine, the distribution parameter α depends only on the number of lactoglobulin molecules in solution. It also shows that for a fixed concentration of lactoglobulin, α decreases as the glycine concentration increases. This behavior suggests that glycine acts to decrease the interaction between lactoglobulin molecules and parallels the well-known action of glycine to increase the solubility of lactoglobulin in water.

The foregoing discussion has shown that the character of the dielectric constant dispersion of β-lactoglobulin solutions is affected by the concentration of protein in the solution and by the concentration of the glycine in the solvent. It has also shown that these concentration effects can be formally described in terms of the parameters α and τ_0 from Eq. (2).

As is well known, the physical properties of a number of proteins in solution apparently change as the concentration of the protein is increased above 0.5 to 1 percent. For example, the sedimentation constant for most proteins decreases with increasing concentration, markedly for nucleohistone, even at 0.1 percent.[18] On the other hand, lactoglobulin in inorganic salt solution showed a barely significant decrease in sedimentation constant even at 4.47 percent protein.[19] It would appear then that lactoglobulin aggregation is not responsible for the observed effects of concentration on dielectric properties unless the behavior of this protein in glycine differs from its behavior in inorganic salt solution. However, a difference in behavior may be considered likely since certain proteins, readily dissolved by neutral salts, are not appreciably dissolved by amino acids such as glycine.[20] Actually, a dipole such as glycine might be expected to be less efficient in suppressing interaction between β-lactoglobulin dipoles than an ionic salt such as sodium chloride, which can supply positive and negative ions to the negative and positive poles of the dipole, respectively, by ionic interchange, whereas the glycine carries along physically an equal and opposite charge.

Ferry and Oncley[21] measured the dielectric dispersion of serum albumin in concentrations ranging up to 5.1 percent and for serum pseudoglobulin in concentrations ranging up to 2.4 percent. Although the dispersion curves did not correspond to the spherical Debye curve, no marked change in the shape of the dispersion curves or in the relaxation time occurred with increasing concentration. On the other hand, the data of Arrhenius[22] for hemoglobin (concentrations approximating 3 percent, except for one

[18] R. O. Carter, J. Am. Chem. Soc. **63**, 1960 (1941).

[19] K. O. Pedersen, Biochem. J. **30**, 964 (1936).

[20] E. J. Cohn, page 619, reference 15.

[21] J. D. Ferry and J. L. Oncley, J. Am. Chem. Soc. **60**, 1123 (1938).

[22] S. Arrhenius, Nova Acta Reg. Soc. Sci. Upsaliensis [IV] **12**, No. 5 (1940).

TABLE I. Dielectric constants of lactoglobulin liquid crystals (32.4 percent protein).

Frequency, ν (megacycles)	Dielectric constant, ϵ'		
	13.7°C	16.6°C	20.0°C
5.00	69.0	69.3	70.9
4.00	70.3		71.4
3.00	71.6	69.9	70.9
2.00	73.3		71.7
1.00	80.6	76.0	73.9
0.800	79.6		75.0
0.600	83.0	81.8	77.5
0.500	84.0		80.4
0.400	84.8	85.8	83.9
0.300	87.8		87.1
0.200	93.3	93.5	94.2
0.100	109.0		108.0
0.0800	113.3	118.2	115.3
0.0600	123.6		127.6
0.0500	128.1	136.1	136.3
0.0400	139.1		148.3
0.0300	151.1	163.1	168.0
0.0200	178.1		200.9
0.0100	250.3	266.1	282.6

TABLE II. Dielectric increments and dipole moments for β-lactoglobulin dissolved in aqueous glycine. Dipole moments based on Eq. (6).

Glycine concentration (moles)	Lactoglobulin concentration C (g/l)	$(\epsilon_0-\epsilon_\infty)$	$\left(\frac{\epsilon_0-\epsilon_\infty}{C}\right)$	μ (e.s.u.)
0.48	3.48	6.5	1.87±0.3[1]	784×10^{-18}
	10.4	19.2	1.84±0.1	775
	20.9	33.0	1.58±0.05	575
1.5	12.7	25.5	2.01±0.07	810
	21.2	38.2	1.80±0.05	766
	38.2	67.3	1.76±0.03	758
	63.7	118.2	1.86±0.01	781
2.5	11.8	25.8	2.18±0.09	844
	23.5	51.9	2.21±0.04	850
	47.0	93.0	1.98±0.02	805
	70.5	126.5	1.80±0.01	766
	94.0	167.3	1.78±0.01	764

[1] Estimated probable error in dielectric increment.

experiment where the concentration was 9 percent) compared with the data of Oncley[4] for hemoglobin (concentration 0.4 to 1.4 percent) suggests a concentration effect similar to that reported here for lactoglobulin. Arrhenius reported a relaxation time approximately twice that reported by Oncley. In fact, such a concentration effect would bring their results into accord. The results of Johnston and Williams,[23] however, show a concentration effect for nitrobenzene dissolved in oil. The proportional increase in the relaxation time observed by these authors for a change in concentration from 4 to 8 percent is about the same as that found for lactoglobulin for the same change in concentration. Unfortunately, the shapes of the dispersion curves for nitrobenzene are uncertain because it was not possible to make measurements in the high frequency region.

The concentration effects found for the dielectric properties of lactoglobulin solutions apparently reflect the effects of concentration on the interaction between individual lactoglobulin molecules. However, since the sedimentation constant is so slightly affected by concentration, the following questions arise: (1) are the dielectric properties of lactoglobulin more sensitive to concentration effects than other physical properties (sedimentation constant, diffusion constant, osmotic pressure, etc.), and (2) are the properties of lactoglobulin in glycine solution markedly different from the properties in organic salt solution?

Dispersion—Liquid Crystals

The dielectric constants of β-lactoglobulin liquid crystals are presented in Table I. No values of the loss factor were obtained for the liquid crystals owing to the fact that measurements of the a.c. conductivity were not made at sufficiently low frequencies to determine G_0 and thus permit calculation of ϵ'' according to Eq. (1). The lack of values of ϵ'' precluded a test of Eq. (2) on the basis of the ϵ'' *versus* ϵ' plot as was done for the β-lactoglobulin solutions in glycine. By successive trials, however, Eq. (3) has been fitted to the data given in Table I for the liquid crystals at

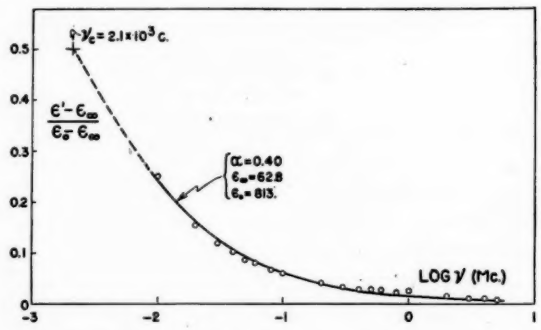

FIG. 9. Frequency variation of dielectric constant, according to Eq. (3), for liquid crystals containing 324 grams per liter of β-lactoglobulin. The data shown are for 13.7°C.

[23] J. H. L. Johnston and J. W. Williams, Phys. Rev. 34, 1483 (1929).

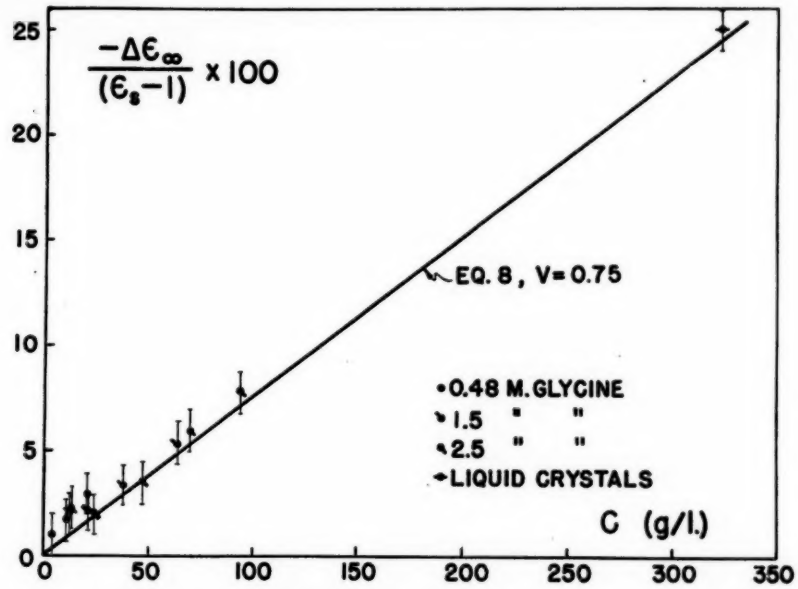

FIG. 10. Dependence of infinite frequency dielectric constant ϵ_∞ on lactoglobulin concentration C. The curve was calculated according to Eq. (8) with $v=0.75$ cc per gram. $\Delta\epsilon_\infty=(\epsilon_s-\epsilon_\infty)$.

13.7°. The resulting curve is shown in Fig. 9. It is estimated that a change of ±5 percent in any one of the four parameters ϵ_0, ϵ_∞, τ_0 and α of Eq. (3) is sufficient to destroy the agreement between the experimental data and Eq. (3). It is noteworthy that the values of $\tau_0=7.6\times10^{-5}$ sec. and $\alpha=0.40$ for the liquid crystals are considerably larger than the corresponding values for the most concentrated solutions of β-lactoglobulin in glycine.

The dielectric constants of the liquid crystals at 16.6° and 20.0°C differ only slightly at most frequencies from the values obtained at 13.7°C. The greatest differences occur at the lowest frequencies, as is shown in Table I, and amount to a maximum increase in ϵ' at 0.01 Mc of 6 percent (at 16.6°C) and 12 percent (at 20.0°C).

In view of these small differences in ϵ', no attempt was made to fit Eq. (3) to the data for the higher temperatures. No claim of great accuracy is made for the values of ϵ_0, ϵ_∞, τ_0, and α found for the 13.7° data. However, the values given are consistent as to (1) the width of the frequency region of the dispersion of ϵ', and (2) the order of magnitude of the dielectric increments and the relaxation times found for the more concentrated solutions of lactoglobulin in glycine.

The liquid crystals furnish an example of a system of β-lactoglobulin in which considerable molecular interaction may be presumed to occur. The extreme values of α and τ_0 found for this material would appear to support the suggestion made above that the type of dielectric dispersion observed for the glycine solutions of β-lactoglobulin is caused by interaction between lactoglobulin molecules.

Dipole Moment

The dipole moment of the β-lactoglobulin molecule can be *estimated* from the dielectric increment $(\epsilon_0-\epsilon_\infty)$ by means of the empirical equation, described by Oncley,[4]

$$\mu=A[M(\epsilon_0-\epsilon_\infty)/C]^{\frac{1}{2}}. \qquad (6)$$

Here μ is the dipole moment in e.s.u., A is a constant equal to 2.86×10^{-18} at 20°C, and M is the molecular weight (40,000 for β-lactoglobulin).

A summary of the values of the dielectric increment obtained from the circle diagrams of Figs. 2–4 is given in Table II. Values of the dipole moment obtained from Eq. (6) are also shown.

An examination of the dipole moments in Table II reveals an apparent tendency for the dipole moment to increase with increasing con-

centrations of glycine in the solvent and for the moment to decrease with increasing lactoglobulin concentration. As is indicated in Table II the dielectric increments for the lower concentrations of lactoglobulin are subject to relatively large probable errors. It was noted previously that the observed dielectric constants are subject to a probable error of about ± 0.5 unit, and in addition to this possible uncertainty, the possibility of errors in values of ϵ_0 and ϵ_∞, which were obtained by extrapolation (Figs. 2–4), must be considered. If the value of μ obtained for $C=20.9$ is discarded as being entirely too small, the other values of μ may be represented by a mean value of 791×10^{-18} e.s.u. with an average deviation of $\pm 26\times10^{-18}$ e.s.u. This value of μ is somewhat larger than the value reported by Ferry and Oncley.[1] These authors obtained values of μ equal to 730 and 770 at 25 and 0°C, respectively. By interpolation $\mu=738$ at 20°C. A possible explanation for the lower value of μ obtained by Ferry and Oncley may lie in the method of obtaining ϵ_0 used by them. Values of ϵ_0 were taken as the average of ten values of ϵ' in the frequency range 0.010 to 0.080 Mc. This procedure is based upon the fact that they were able to detect no dispersion of the dielectric constant for frequencies less than 0.10 mc. It appears that any error introduced by their procedure would tend to give too small values of ϵ_0 and thus of μ.

The values of ϵ_∞ used by Ferry and Oncley were calculated on the assumption that the volume of the solution occupied by the lactoglobulin molecules does not contribute appreciably to the dielectric polarization at frequencies lying beyond the dispersion region. As will be shown below, values of ϵ_∞ obtained in this manner agree well with the values of ϵ_∞ obtained by extrapolation using the circle diagram method.

If it is assumed that the high frequency dielectric constant ϵ_∞ of a protein solution is contributed principally by the solvent molecules and that the volume occupied by the protein has a high frequency dielectric constant of unity, then

$$(\epsilon_\infty-\epsilon_s)=(\epsilon_s-1)vC/1000 \qquad (7)$$

or

$$(\epsilon_\infty-\epsilon_s)/(\epsilon_s-1)=vC/1000, \qquad (8)$$

where v is the specific volume of the protein and ϵ_s is the dielectric constant of the solvent. This equation is subject to question from the lack of the true high frequency dielectric constant of the protein and of the degree of hydration of the protein in solution. The equation has been fully discussed by Oncley.[24] A graph of Eq. (8) is given in Fig. 10. The graph has been drawn for $v=0.75$ cc/g. On the graph are plotted values of $(\epsilon_\infty-\epsilon_s)/(\epsilon_s-1)$ for the solutions of β-lactoglobulin and for the β-lactoglobulin liquid crystals. The extrapolated values of ϵ_∞ for the glycine solutions were obtained from the high frequency extrapolation of the circle diagrams of Figs. 2–4. The value of ϵ_∞ for the liquid crystals was obtained from Fig. 9 as discussed previously.

It is seen that within the estimated limits of error the values of ϵ_∞ obtained by extrapolation by the circle diagram method and by means of Eq. (8) are in good agreement.

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[24] J. L. Oncley, in Chapter 22, of J. T. Edsall and E. J. Cohn, *Proteins, Amino Acids, and Peptides* (Reinhold Publishing Corporation, New York, 1943).

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Note on Becker's Theory of the Shock Front

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Becker, in a classical paper, concludes that weak shocks are many free paths thick and may be treated by ordinary hydrodynamics including the effects of viscosity and thermal conductivity of the medium; that moderately strong shocks have a thickness of the order of a free path and must be treated by a direct attack on the relevant Boltzmann equation; while violent shocks have a thickness small compared with a free path and even the Boltzmann equation is no longer applicable. It is shown here that this last conclusion rests on an oversight; the thickness of a shock front is always at least of the order of magnitude of a free path, and it is to be expected that the Boltzmann equation can be applied even for the most violent shocks.

INTRODUCTION

VISCOSITY and heat conduction are often neglected in the equations of motion of a compressible fluid. The researches of Earnshaw[1] and Riemann[2] showed that a continuous solution of the resulting equations may be impossible for longer than a finite time if an initial disturbance moves from high to low pressure. The velocity of sound being greater at greater temperature produced by adiabatic compression, a disturbance on the high pressure side moves faster than on the low, and the disturbance becomes more and more concentrated, until finally no continuous solution is possible. Physically, a shock wave has been built up. The subsequent motion of the shock front may be obtained by regarding it as a surface of discontinuity across which there is continuous flow of mass and momentum, leading to equations given by Stokes[3] and later by Rankine.[4] In order that energy also should be conserved the entropy must increase across the front leading to a further condition owing to Huguoniot.[5] (A rarefaction shock, across which entropy would have to diminish, is therefore not possible.)

It was explained by Rankine and later by Rayleigh[6] and by Taylor[7] that if viscosity and heat conduction are taken into account, the shock wave would never become an infinitely sharp discontinuity, but would have a finite thickness (3×10^{-5} cm for moderately strong shock waves in air). Becker,[8] in a classical paper, obtained the exact solution of these equations for a one-dimensional stationary shock wave in a simple gas. He found that for a violent shock ($p_2/p_1=8$, where p_2 and p_1 are the pressures on opposite sides of the shock), the thickness for a gas was of the order of a mean free path (10^{-5} cm). The equations of hydrodynamics may be derived from kinetic theory only provided that large macroscopic changes do not occur over a distance of the order of a free path. Becker therefore concludes that these equations would not apply within a moderately violent shock, and that recourse must then be had to a direct solution of the Boltzmann equation of kinetic theory.

Becker finds further that for a very violent shock ($p_2/p_1=2000$) the thickness of the shock wave on the basis of these (inapplicable) equations is so much smaller yet as to approach the average intermolecular distance (3×10^{-7} cm) and he inferred that the same order of magnitude holds for liquids. He therefore doubts even the applicability of the Boltzmann equation to very violent shocks.

Unfortunately Becker overlooks the increase of the coefficients of thermal conductivity and of viscosity with increasing temperature and pressure, using the values for normal temperature and pressure as constants. If this oversight is corrected the hydrodynamical equations never lead to a thickness small compared to the length

* On leave of absence from Ohio State University.
[1] S. Earnshaw, Phil. Trans. **150**, 133 (1858).
[2] B. Riemann, Gott. Abh. **8**, 43 (1858).
[3] E. E. Stokes, Phil. Mag. **3**, 23, 349 (1848).
[4] W. V. M. Rankine, Phil. Trans. **160**, 277 (1870).
[5] A. Hugoniot, J. École Poly. 58, (1889).
[6] Lord Rayleigh, Proc. Roy. Soc. **A84**, 371 (1910).
[7] G. I. Taylor, Proc. Roy. Soc. **A84**, 371 (1910).
[8] R. Becker, Zeits. f. Physik **8**, 321 (1922).

of a free path. Thus the ordinary approximation of the kinetic theory of non-uniform gases is valid for the less violent shocks and leads to the equations of hydrodynamics without viscosity and heat conduction as a first approximation, including these in the second approximation, in which approximation Becker's solution is obtained. The coefficients of the terms required for the third approximation have been given by Burnett.[9] The inclusion of these terms leads to an even greater thickness, but the numerical values indicate that the series of approximations may not converge for very violent shocks, for which the departure from a Maxwellian distribution of velocities at points within the shock front may be large. However, methods similar to those of Milne[10] and Hopf[11] for the transfer of radiation through the solar photosphere are still available for solving the Boltzmann equation.

THE EQUATIONS OF HYDRODYNAMICS AS OBTAINED FROM KINETIC THEORY[12]

For steady motion in one dimension (x) the equations of continuity, momentum, and energy, are obtained from kinetic theory in the form

$$u\frac{d\rho}{dx}=-\rho\frac{du}{dx}, \tag{1}$$

$$u\frac{d}{dx}\rho u=-\rho u\frac{du}{dx}-\frac{d}{dx}p, \tag{2}$$

$$u\frac{d}{dx}E=-E\frac{du}{dx}-p\frac{d}{dx}u-\frac{d}{dx}q, \tag{3}$$

where u is the mean molecular velocity in the x direction, ρ is the density, E is the energy per unit volume referred to axes moving with velocity u, p is the mean rate of flow of momentum in the x direction per unit area perpendicular to the x direction referred to these axes, and q is the mean rate of flow of energy defined similarly.

These equations have the first integrals[8]

$$\rho u=a, \tag{4}$$

$$au+p=b, \tag{5}$$

$$uE+ub-\tfrac{1}{2}au^2+q=c, \tag{6}$$

expressing that the rates of flow of mass, momentum, and energy, in the x direction, are the same for all values of x.

These integrated equations must hold generally and show that, provided there exists a solution of the Boltzmann equation corresponding to steady flow from uniform steady motion for large negative x to uniform steady conditions for large positive x, the relation between these uniform conditions is that given by the Rankine-Hugoniot equations to which these equations lead.

The usual first approximation of kinetic theory gives, for a gas with energy only of molecular translation,

$$\rho=nm,\quad E=\tfrac{3}{2}nkT,\quad p=p^{(0)}=nkT,\quad q=0, \tag{7}$$

where n is the number of molecules per unit volume, T is the absolute temperature, k is Boltzmann's constant, and m is the mass of a molecule.

The methods of Chapman and Enskog, using $\rho=nm$, $E=\frac{3}{2}nkT$ (the latter essentially as a definition of T), lead to a solution of Boltzmann's equation by successive approximation in series giving

$$\begin{aligned}p&=p^{(0)}+p^{(1)}+p^{(2)}+\cdots,\\ q&=q^{(1)}+q^{(2)}+\cdots,\end{aligned} \tag{8}$$

where, in the one-dimensional case,[12]

$$p^{(0)}=nkT,\quad p^{(1)}=-\frac{4}{3}\mu\frac{du}{dx},\quad q^{(1)}=-\lambda\frac{dT}{dx}, \tag{9}$$

$$\begin{aligned}p^{(2)}=\tilde{\omega}_1\frac{\mu^2}{p^{(0)}}\frac{du}{dx}\frac{2}{3}\frac{du}{dx}+\tilde{\omega}_2\frac{\mu^2}{p^{(0)}}\Big\{-\frac{2}{3}\frac{d}{dx}\Big(\frac{1}{\rho}\frac{dp^{(0)}}{dx}\Big)\\ -\frac{2}{3}\Big(\frac{du}{dx}\Big)^2-\frac{8}{9}\Big(\frac{du}{dx}\Big)^2\Big\}+\tilde{\omega}_3\frac{\mu^2}{\rho T}\frac{2}{3}\frac{d^2T}{dx^2}\\ +\tilde{\omega}_4\frac{\mu^2}{\rho p^{(0)}T^2}\frac{2}{3}\frac{dp^{(0)}}{dx}\frac{dT}{dx}\\ +\tilde{\omega}_5\frac{\mu^2}{\rho T^2}\frac{2}{3}\Big(\frac{dT}{dx}\Big)^2+\tilde{\omega}_6\frac{\mu^2}{p^{(0)}}\Big(\frac{du}{dx}\Big)^2,\end{aligned}$$

[9] E. S. Burnett, Proc. Lond. Math. Soc. **39**, 385 (1935).
[10] E. A. Milne, M. N. R. A. S. **88**, 493 (1928).
[11] E. Hopf, "Mathematical problems of radiative equilibrium," *Cambridge Tracts in Mathematics and Mathematical Physics* (Cambridge University Press, Cambridge, England, 1934).
[12] S. Chapman and T. E. Cowling, *Mathematical Theory of Non-Uniform Gases* (Cambridge University Press, Cambridge, England, 1939), Chapters 3, 7, 15.

$$q^{(2)}=\vartheta_1\frac{\mu^2}{\rho T}\frac{du}{dx}\frac{dT}{dx}+\vartheta_2\frac{\mu^2}{\rho T}\left\{\frac{2}{3}\frac{d}{dx}\left(T\frac{du}{dx}\right)+2\frac{du}{dx}\frac{dT}{dx}\right\}+\vartheta_3\frac{\mu^2}{\rho p^{(0)}}\frac{dp^{(0)}}{dx}\frac{2}{3}\frac{du}{dx}+\vartheta_4\frac{\mu^2}{\rho}\frac{d}{dx}\left(\frac{2}{3}\frac{du}{dx}\right)+\vartheta_5\frac{\mu^2}{\rho T}\frac{dT}{dx}\frac{2}{3}\frac{du}{dx}, \quad (10)$$

where μ is the coefficient of viscosity, λ the coefficient of thermal conductivity, the forms of which have been computed for various laws of interaction between the molecules.

The coefficients $\vartheta_1, \cdots, \vartheta_5$, and $\bar{\omega}_1, \cdots, \bar{\omega}_6$, have been evaluated for molecules attracting according to an inverse fifth power law:[9]

$$\vartheta_1=75/8, \quad \vartheta_2=45/8, \quad \vartheta_3=-3, \quad \vartheta_4=3, \quad \vartheta_5=6, \quad (11)$$

$$\bar{\omega}_1=10/3, \quad \bar{\omega}_2=2, \quad \bar{\omega}_3=3, \quad \bar{\omega}_4=0, \quad \bar{\omega}_6=3, \quad \bar{\omega}_6=8. \quad (12)$$

The coefficients $\bar{\omega}_1, \cdots, \bar{\omega}_6$, have also been evaluated for rigid elastic spheres.

Successive approximations to the solution of the Boltzmann equation may now be obtained from Eqs. (4)–(6), by using only the terms $p^{(0)}+p^{(1)}$ and $q^{(1)}$; or only the terms $p^{(0)}+p^{(1)}+p^{(2)}$ and $q^{(1)}+q^{(2)}$; and so on; and subject to the convergence of this process, a solution of the Boltzmann equation of the desired form would be obtained.

For a gas made up of molecules with internal degrees of freedom this is not entirely correct; energy does not partition itself immediately into the internal degrees of freedom. Bethe and Teller[13] have given arguments which show that while energy passes rapidly to rotation of the molecules, it passes only slowly to internal vibration. Through the shock front itself, when of only a few mean-free-paths thickness, we need take account only of the molecular rotation. The shock front is then followed by a region in which the energy is gradually distributed until the equilibrium state is reached.

Through the shock front it would still be necessary, strictly, to take account of the delay in exchanging with molecular rotation. In the only such case for which the theory of non-uniform gases has been worked out, that of rough spherical molecules, the first approximation departs little from what would be obtained by taking the equations (4)–(6), with

$$E=\tfrac{1}{2}NnkT, \quad \lambda=f\mu\frac{kN}{2m}, \quad (13)$$

where N is the number of effective degrees of freedom (3 for monatomic, 5 for diatomic, and 6 for polyatomic molecules) and f is a constant ($\approx\frac{1}{4}(9\gamma-5)$ where $\gamma=(N+2)/N$ is the ratio of specific heats.

Finally, when we require the variation of μ with temperature, we have, for elastic spheres of diameter σ,

$$\mu=\frac{v}{\pi^{\frac{1}{2}}}\frac{(kmT)^{\frac{1}{2}}}{\sigma^2}, \quad (14)$$

where $v=0.998$, while the mean free path l is given by

$$l=1/\sqrt{2}\pi n\sigma^2. \quad (15)$$

The variation of μ with temperature for actual gases is given more nearly by a formula of Sutherland's type, but this gives variation of the above form at high temperatures.

BECKER'S THEORY OF THE THICKNESS OF SHOCK FRONTS[8]

If in Eqs. (4)–(6), we replace p by $p^{(0)}+p^{(1)}$, i.e., $nkT-(4/3)\mu(du/dx)$, and q by $q^{(1)}$, i.e., $-\lambda(dT/dx)$, they may be regarded as equations to determine du/dx and dT/dx in terms of u and T. Making the substitutions

$$u=\frac{b}{a}\omega, \quad T=\frac{m}{k}\frac{b^2}{a^2}\theta \quad (16)$$

and writing

$$\lambda=f\mu\frac{kN}{2m},$$

these become Becker's equations

$$\frac{1}{a}\frac{4}{3}\mu\frac{d\omega}{dx}=\omega+\frac{\theta}{\omega}-1, \qquad \frac{1}{a}f\mu\frac{d\theta}{dx}=\theta-\delta[(1-\omega)^2+\alpha], \quad (17)$$

[13] H. A. Bethe and E. Teller, "Deviations from thermal equilibrium in shock waves" (unpublished).

where

$$\delta=\frac{1}{N},\quad \alpha=\frac{2ac}{b^2}-1,$$

which give

$$\frac{d\theta}{d\omega}=\frac{4}{3f}\frac{\theta-\delta[(1-\omega)^2+\alpha]}{\omega^2-\omega+\theta} \tag{18}$$

to determine the variation of θ with ω across the shock.

Following Becker the solution of this equation for which x extends from $-\infty$ to ∞ extends from $\theta_1=\omega_1(1-\omega_1)$ to $\theta_2=\omega_2(1-\omega_2)$, where

$$\omega_1+\omega_2=\frac{N+2}{N+1},\quad \omega_1\omega_2=\frac{2ac/b^2}{N+1}.$$

In case

$$\frac{3}{4}f=1+\frac{2}{N},$$

this special solution has the simple form

$$\theta=\frac{1}{N+2}\left(\frac{2ac}{b^2}-\omega^2\right)$$
$$=\frac{\theta_1\omega_2^2-\theta_2\omega_1^2}{\omega_1^2-\omega_2^2}-\frac{\theta_2-\theta_1}{\omega_1^2-\omega_2^2}\omega. \tag{19}$$

For air $N=5$, $f=1.95$ (observed); if we take $f=1.86$, following Becker, we have this simple case, and we may expect this change of f to make only small differences in the result.

Thus far, according to Becker: To find the thickness of the shock front, however, for violent shocks, for which there is considerable change of pressure and temperature, it is essential to take account of the increase of viscosity and thermal conductivity with temperature.

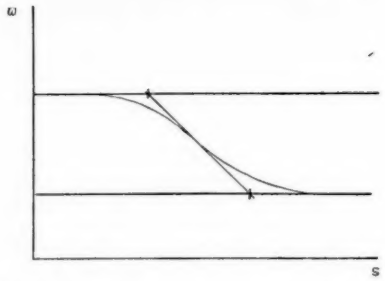

FIG. 1. Definition of "thickness" of the shock front.

Using (14) and (15), if we measure "distance" in terms of "free paths," i.e., in terms of s where

$$\frac{ds}{dx}=l, \tag{20}$$

we replace Becker's equations (17) by

$$\frac{4}{3}\left(\frac{2}{\pi}\right)^{\frac{1}{2}}\nu\frac{\sqrt{\theta}}{\omega}\frac{d\omega}{ds}=\omega+\frac{\theta}{\omega}-1,$$
$$f\left(\frac{2}{\pi}\right)^{\frac{1}{2}}\nu\frac{\sqrt{\theta}}{\omega}\frac{d\theta}{ds}=\theta \tag{21}$$
$$-\frac{1}{N}\left[(1-\omega)^2+\left(\frac{2ac}{b^2}-1\right)\right].$$

We may measure the thickness of the shock front by the whole change in ω divided by the greatest slope $d\omega/ds$ (Fig. 1).

$$(\omega_1-\omega_2)\left(\frac{ds}{d\omega}\right)_{\min}=\frac{4}{3}\left(\frac{2}{\pi}\right)^{\frac{1}{2}}\nu\left\{\frac{(\omega_1-\omega_2)[(\omega_1+\omega_2)(\omega_1\omega_2-(\omega_1+\omega_2-1)\omega^2)]^{\frac{1}{2}}}{(\omega_1-\omega)(\omega-\omega_2)}\right\}_{\min}. \tag{22}$$

This thickness, as well as the maximum value of $p^{(1)}/p^{(0)}$ in the front,

$$\left(\frac{p^{(1)}}{p^{(0)}_{\max}}=-\frac{4}{3}\frac{\mu}{p}\frac{du}{dx}\right)_{\max}$$
$$=-\left\{\frac{(\omega^2-\omega)(\omega_1+\omega_2)}{\omega^2(1-\omega_1-\omega_2)+\omega_1\omega_2}+1\right\}_{\max} \tag{23}$$

is given for shocks of various intensity in Table I.

If now the expressions (17) for $d\omega/dx$ and $d\theta/dx$ are modified by including $p^{(2)}$ and $q^{(2)}$ evaluated from the above solution on the right-hand sides, they give

$$\frac{1}{a}\frac{4}{3}\mu\frac{d\omega}{dx}=\left(\omega+\frac{\omega}{\theta}-1\right)\Big/\left(1+\frac{p^{(2)}}{p^{(1)}}\right),$$
$$\frac{1}{a}f\mu\frac{d\theta}{dx}=[\theta-\delta\{(1-\omega)^2+\alpha\}]\Big/\left(1+\frac{q^{(2)}}{q^{(1)}}\right), \tag{24}$$

TABLE I.

$\frac{p_2}{p_1}$	$\frac{\rho_2}{\rho_1}$	$\frac{T_2}{T_1}$	Thickness (free paths)	$\frac{p^{(1)}}{p^{(0)}}$
1.0000	1.0000	1.0000	∞	0.0000
2.6661	4.4981	1.6871	3.98	0.3460
3.7899	9.8365	2.5954	3.08	0.7198
4.6382	19.700_3	4.2474	2.25	1.0967
5.2931	43.387_6	8.1998	1.98	1.4854
6.0000	∞	∞	1.74	2.5000

where, from Burnett's formulae, (9)–(12),

$$p^{(2)}/p^{(1)} \approx p^{(1)}/p^{(0)},$$

and

$$q^{(2)}/q^{(1)} \approx 10p^{(1)}/p^{(0)}.$$

We see that, while there is no guarantee of convergence, the general effect of the third-order terms is to make the front thicker.

Lastly, in the notation of kinetic theory, the Boltzmann equation, the solutions of which we are approximating, is

$$u\frac{\partial f}{\partial x} = \int\int\int\int (f'f_1' - ff_1)gbdbd\epsilon dv_1 du_1$$

to determine $f(x, u, v)$ and, if the method of Chapman and Enskog fails to converge, this may be rewritten

$$u\frac{\partial f}{\partial x} + f\int\int\int\int f_1 gbdbd\epsilon dv_1 du_1 = \int\int\int\int f'f_1' gbdbd\epsilon dv_1 du_1$$

and may be approximated by iteration using an already determined approximation both on the right-hand side and in the integral on the left, in the manner used in astrophysics for the transport of radiation in a stellar photosphere.[10 11]

CONCLUSIONS

All shock waves in air but the weakest are a few free paths thick. If the shock is strong the approximation process of the theory of non-uniform gases probably does not converge, because the distribution function of molecular velocities within the front departs too far from the Maxwellian. There is, however, no reason to doubt that the Boltzmann equation possesses a suitable solution.

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The Charge Effect in Photographic Development: Role of the Gelatin*

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The approach of negatively charged developer ions to the surface of a silver bromide grain is opposed by charge barriers originating both with the gelatin and with the adsorbed bromide ions. It is shown that the effect of neutral salt upon the rate of development by negative ions results primarily from a depression of the gelatin charge barrier. The effect of salt upon the bromide barrier is relatively unimportant. On the other hand, a change in the bromide barrier is mainly responsible for certain other kinetic effects, such as the induction period in development and the accelerating action of phenosafranin.

A COLLOIDAL particle of silver bromide, suspended in a solution containing excess soluble bromide, is negatively charged by the adsorption of excess bromide ions to the surface. This charge acts to concentrate positive ions in the solution near the surface and to oppose the approach of other negative ions to the surface. The resulting electric double layer consists on the one hand of the adsorbed bromide-ion layer, together with a more or less firmly held water shell, and on the other hand a diffuse ionic atmosphere in which positive ions predominate near the solid surface but decrease in predominance as the distance from the surface increases.

If the system is placed in an electric field, the

* Communication No. 994 from the Kodak Research Laboratories.

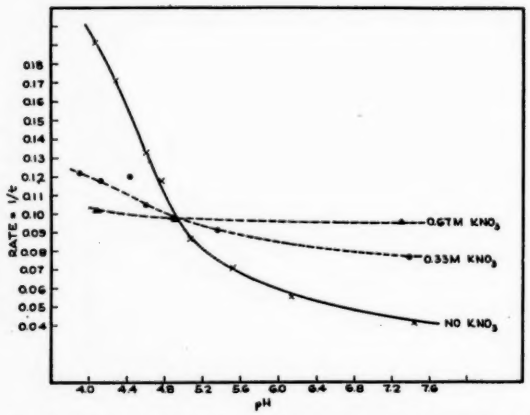

FIG. 1. Effect of KNO_3 on development by $Fe(C_2O_4)_2^=$. $\triangle = 0.67\ M$ KNO_3; $\circ = 0.33\ M$ KNO_3; $\times$ = No KNO_3.

particle moves through the solution. The mobility of the particle is determined by the potential at the surface of shear between the particle and the bulk solution, i.e., the zeta-potential. For a given concentration of bromide ions in the adsorbed layer, the potential at any point in the solution near the adsorbed layer depends markedly upon the ion concentration in the solution. The higher the ion concentration, the greater will be the crowding of positive ions near the solid surface, and hence the lower the potential in this region or at the shear surface itself.

In the presence of gelatin, the silver bromide particle becomes coated with an adsorbed layer of gelatin which is tenaciously held to the surface.[1] It is not known to what extent the gelatin displaces the adsorbed bromide and water layer, and to what extent it simply forms an additional outer coating. However, the behavior of the particle in an electric field is now determined by the gelatin and not the bromide layer. On the positive side of the gelatin isoelectric point, the particle moves as a positively charged body; on the negative side, it moves as a negatively charged body.[2] The surface of shear is between the gelatin layer and the solution.

The sensitive layer of the normal photographic material consists fundamentally of tiny crystals of silver halide (the grains) embedded in a layer of gelatin. These crystals are prepared and aged in the presence of excess halide and gelatin, so that adsorbed layers of each should form as in the case of the colloidal silver bromide particle just discussed. The adsorbed gelatin layer is now surrounded, however, by bulk gelatin instead of by solution.

In normal "chemical," or contact development of the photographic layer, the reaction takes place at the interface between the silver halide and silver (either from latent image or previous development). The developing agent accordingly must penetrate to the grain surface before reaction can take place. Many of the developing agents are active only in the form of negatively charged ions. In such cases, it has already been shown[3] that the potential in the vicinity of the grain surface exerts a pronounced influence upon the kinetics of development.

In previous investigations of this charge effect, development was always carried out in alkaline solution at a *p*H well above the isoelectric point of the gelatin. Accordingly, both the bromide layer and the gelatin could contribute to a charge barrier resisting the approach of the developer ions to the surface of the silver bromide grain. The existing data on the effect consisted largely of measurements of the change in rates of development produced by the addition of bromide, various dyes, and neutral salts to the developer solution. Certain other development characteristics, particularly the existence and magnitude of the induction period, were also shown to depend upon the charge of the developer ion rather than upon the chemical nature of the agent. These data seemed to be largely explicable on the basis of the bromide charge

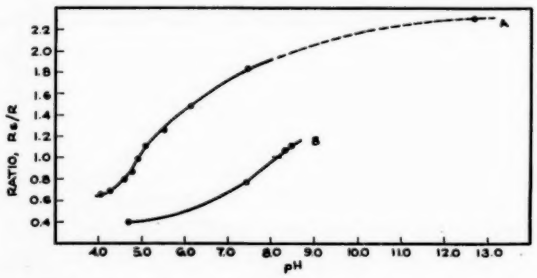

FIG. 2. Salt effect in terms of ratio of rates in presence and absence of 0.33 M KNO_3. Curve A is for film with a gelatin of isoelectric point = 4.9; curve B is for film with a gelatin of isoelectric point = 8.

[1] S. E. Sheppard, R. H. Lambert, and R. L. Keenan, J. Phys. Chem. **36**, 174 (1932).

[2] Cf. L. F. Tice and W. G. Batt, Am. J. Pharmacy **109**, 29 (1937).

[3] T. H. James, J. Phys. Chem. **43**, 701 (1939).

alone,[3,4] but a hint of some action of the gelatin was contained in observations on the behavior of the ferro-oxalate developer in acid solution.[3] Recently, however, it has been shown[5] that negatively charged gelatin layers exert a definite restraining action on the penetration of negatively charged dye ions, and hence might be expected to exert a similar action upon the penetration of developer ions. The resistance to the penetration of the dye ions was largely removed by the addition of large amounts of neutral salt, and Sheppard has suggested[6] that a similar action can account, at least in part, for the increase in rate of development produced by adding neutral salts to solutions of ionic developing agents.[7]

In the present paper, it will be shown that a change in the electric barrier of the gelatin is almost entirely responsible for the acceleration produced by neutral salt. The slight effect of salt upon the bromide barrier can be measured by working at the isoelectric point of the gelatin. By following this procedure further, it can be shown that the bromide barrier is primarily responsible for the induction period and for certain other kinetic effects, such as the accelerating action of phenosafranin.

MATERIALS AND PROCEDURE

Two distinct photographic materials were employed. The first (*A*) was a normal motion-picture positive film prepared from gelatin which had an isoelectric point at about 4.9. The second (*B*) was a positive-type film prepared from an acid-process gelatin which had its isoelectric point at about 8. The light-sensitive material in each case was silver bromide.

As a developer, the bivalent ferro-oxalate is well suited to the purpose of the investigation. The oxidation product produces no complicating kinetic effects under the experimental conditions employed. The developer can be used in acid, neutral, and slightly alkaline solution. Thus, development can be carried out on either side of the isoelectric point of the gelatin. The bivalent iso-ascorbic acid ion was used as developer in the highly alkaline region, since in this case also the oxidation product does not complicate the development kinetics.[8]

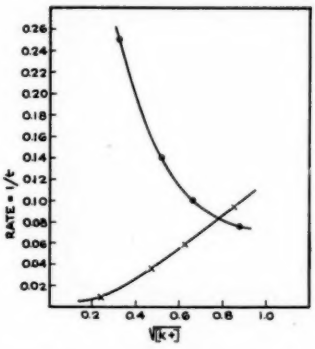

FIG. 3. Salt effect on film with gelatin isoelectric point of approximately 8. $-\bigcirc-\bigcirc-$ = pH = 4.7; log E = 1.45; $-\times-\times-$ = pH = 12.7; log E = 1.75.

The ferro-oxalate developer contained 0.005 *M* ferro-oxalate and 0.04 *M* excess potassium oxalate. The pH of the solution was adjusted by adding the required amount of sulfuric acid for pH values of less than 7.5, and borax for higher values. The concentration of iso-ascorbic acid was 0.005 *M* in a solution containing 0.04 *M* potassium hydroxide. The developers were prepared from oxygen-free component solutions, and all development operations were carried out in an atmosphere of tank nitrogen which had been freed of oxygen. The apparatus and procedure were essentially those previously described.[3] Development rates were determined in terms of $1/t$ and R, where t is the time required to obtain a fixed, small optical density at a given exposure, and R is the slope of the curve obtained by plotting density against time of development. All values are corrected for fog. Unless otherwise specified, the data recorded here apply to an exposure of log $E = 1.45$, where E is expressed in meter-candle-seconds, t is measured at a density of 0.20, and R at a density of 0.80. Similar results were obtained for other exposure values in the normal exposure range.

[4] F. Urbach, *IX^e Congrès International de Photographie* (Paris, 1935), p. 432. J. E. de Langhe, Zeits. f. wiss. Phot. **35**, 201 (1936). A. Lottermoser and R. Steudel, Kolloid Zeits. **82**, 319; **83**, 37 (1938). T. H. James, J. Phot. Soc. Am. **9**, 62 (1943).

[5] S. E. Sheppard, R. C. Houck, and C. Dittmar, J. Phys. Chem. **46**, 158 (1942).

[6] S. E. Sheppard, "Colloid chemical aspects of photographic development," in *Colloid Chemistry*, edited by J. Alexander (Reinhold Publishing Corporation, New York, 1944), p. 472.

[7] H. Lüppo-Cramer, Kolloid Zeits. **15**, 164 (1914).

[8] T. H. James, J. Am. Chem. Soc. **66**, 91 (1944).

TABLE I. Salt effect in development at the isoelectric point. Ferro-oxalate developer, pH = 4.9, film A.

KBr	KNO_3	$1/t$	R
0.0	0.0	0.099	0.0485
	.33	.098	.048
	.67	.097	.046
.00067	.0	.034	.036
	.67	.036	.041
.0020	.0	.022	.029
	.67	.025	.033

RESULTS AND DISCUSSION

The rate of development of film A in ferro-oxalate decreased with increasing pH, as indicated by the solid curve of Fig. 1. The addition of neutral salt changed the rate of development in most cases, but produced no change at the pH corresponding to the isoelectric point of the gelatin (4.9). The broken curves in Fig. 1 illustrate the effect of potassium nitrate upon the development rate. On the positive side of the isoelectric point, the salt produces a *decrease* in the rate of development; on the negative side, the salt produces the more conventional increase. The three curves, corresponding to no added salt, 0.33 M potassium nitrate, and 0.67 M potassium nitrate, cross at the isoelectric point. Quite similar results were obtained when R was plotted instead of $1/t$.

The absolute rate of development also can be related to the charge of the gelatin. In the absence of salt, increase in the positive charge of the gelatin increases the rate of development, and increase in the negative charge decreases the rate of development. At high salt concentrations, the charge effect of the gelatin is practically eliminated,[5] and the rate of development becomes almost independent of the pH.

As a check on the results obtained with film A, the effect of salt on development of film B was measured. Figure 2 illustrates the results obtained. In this figure, the *ratio* of development rate in the presence of 0.33 M potassium nitrate to that in the absence of added salt is plotted against pH (curve B). The ratio is unity (no salt effect) at a pH of about 8.1. This corresponds well with the isoelectric point of the gelatin used in the preparation of this film. For comparison, results obtained with film A are plotted in the same way (curve A). The point on this curve corresponding to pH = 12.7 is for iso-ascorbic acid instead of ferro-oxalate, but the extension of the curve follows the general shape indicated by the ferro-oxalate points. Thus, the specific properties of the individual developing agents do not appear to be involved in determining the magnitude of the salt effect in these two cases. Only the charge is important.

A series of measurements of the salt effect at various salt concentrations was made at pH = 4.7 with ferro-oxalate and 12.7 with iso-ascorbic acid, using film B as the photographic material. (Data for film A at pH = 12.7 have been given.[8]) The determinations with the ferro-oxalate developer were made in the absence of added bromide, but addition of 0.00667 M potassium bromide to the iso-ascorbic acid developer was necessary to eliminate excessive fog. Results of the determination at the two pH values are given in Fig. 3 as the rate of development, $1/t$, plotted against the square root of the potassium-ion concentration. The salt effect is large in each case, but is opposite in direction.

All of the preceding experiments with ferro-oxalate were carried out in the absence of added bromide. Only the bromide in excess in the original film was present. Under these conditions, the evidence shows clearly that the salt effect is acting exclusively upon the gelatin charge, within the limits of experimental error. This does not, however, preclude an effect upon the bromide when the latter is in considerable excess. Accordingly, measurements in the presence of added bromide were made at the isoelectric point of the gelatin, where the electric barrier of the latter is eliminated. Some results are given in Table I. At the higher bromide concentrations, a

TABLE II. Effect of bromide on development by ferro-oxalate. Film A—no added salt.

pH	KBr	$1/t$	R	Rt
4.76	0.0	0.118	0.054	0.45
	.000167	.071	.052	0.73
	.000667	.044	.049	1.11
	.00167	.030	.039	1.30
4.06	.0	.192	.080	0.42
	.000167	.167	.087	0.52
	.000667	.114	.084	0.76
	.00167	.080	.075	0.94

TABLE III. Effect of phenosafranin. Film *A*; *p*H=4.06; KBr, 0.001667 *M*.

Phenosafranin	1/*t*	*R*
0.0	0.080	0.075
.00002	.105	.084
.00005	.132	.099
.00010	.154	.095
.00020	.192	.100
.00050	.455	.126

small increase in development rate is obtained by increasing the salt concentration. However, the effect is very small in comparison with that observed at similar salt concentrations, but in alkaline solution well to the negative side of the isoelectric point. *The neutral salt acceleration of development, therefore, is caused primarily by an action upon the gelatin charge barrier, even when considerable excess bromide is present.*

It was shown previously[3] that the induction period in development is caused by a charge effect. The original explanation of this effect associated it with a *change* in the adsorbed bromide layer as development progressed. This explanation remains in agreement with the evidence. The induction period persists even on the positive side of the isoelectric point. Moreover, its characteristic sensitivity to the bromide-ion concentration[3, 9] is maintained on the positive side of the gelatin isoelectric point. This is indicated by the data given in Table II. It will be noticed that the $1/t$ rates, which are measured in the induction period region, decrease much more rapidly with increasing bromide concentration than do the R rates, which apply to the region of development beyond the induction period.

[9] T. H. James, J. Phys. Chem. **44**, 42 (1940).

The relative change in $1/t$ with respect to R is indicated by the figures in the last column. The increase in Rt with increasing bromide is not as great at pH=4.06 as at 4.76, probably because of the tendency of the *positive* gelatin layer to counteract to some extent the kinetic effects of the negative bromide barrier. Similarly, the absolute decrease in rate of development with increasing bromide is not as great at the lower pH—a fact which can be explained in the same way. However, the induction period persists at pH=4.06, and the relative extent of the induction period still increases with increasing bromide-ion concentration.

The action of phenosafranin supplies another indication that the bromide barrier is still actively retarding development well to the positive side of the gelatin isoelectric point. This substance increased the rate of development by all of the doubly-charged agents previously studied, and its action is definitely associated with the charge of the developer.[3] In the present investigation, it was observed that phenosafranin accelerates development at the isoelectric point of the gelatin, and indeed well to the positive side of this point. The data in Table III illustrate the effect at pH=4.06, and in the presence of 0.001667 *M* potassium bromide. The acceleration produced by the dye is marked, and comparison with Table II shows that 0.0002 *M* phenosafranin almost completely erased the retarding action which the bromide exerted on development in the absence of the dye. Thus, under the present conditions, approximately one molecule of phenosafranin offsets the retarding effect of eight bromide ions. Approximately the same relation held over the sixteen-fold range of exposures for which data were tabulated.

The Heat Capacity of Gaseous Butadiene-1,3*

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(Received October 20, 1944)

The heat capacity of gaseous butadiene-1,3 at 300°K and at 363°K has been determined by the measurement of the velocity of high frequency sound in the gas over the pressure range from one-third to one atmos. The heat capacity of the gas at zero pressure, evaluated by extrapolation to zero pressure, is in essential agreement with the value calculated from experimental state data. The experimental results are compared with values calculated from spectroscopic and molecular data and a marked disagreement is observed.

INTRODUCTION

THE present paper describes some heat capacity data at 300°K and 363°K obtained by measurements of the velocity of ultrasound in gaseous butadiene-1,3. The purpose of the measurements was to obtain experimental gaseous heat capacity data for comparison with those calculated from spectroscopic and molecular data. The agreement of C_p^0 values

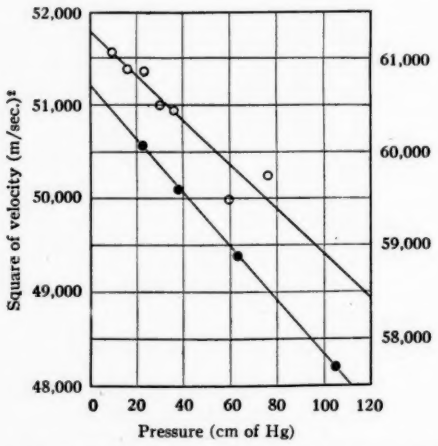

FIG. 1. The velocity of ultrasound in butadiene-1,3. ● and left scale—$t=25.82$°C. ○ and right scale—$t=90.13$°C.

derived from the velocity of ultrasound in the gas at one temperature for several pressures constitutes a verification of the state data used in the computation. In this work we have used state data[1] obtained at the National Bureau of Standards. The results confirm the validity of these data. The comparison of the experimental heat capacities at zero pressure with those from spectroscopic and molecular data will be discussed presently.

MATERIALS

The butadiene used was Dow Chemical Company material obtained from the Petroleum Refining Laboratory of The Pennsylvania State College, through the courtesy of Professor M. R. Fenske.

The butadiene was dried by passing it twice over freshly activated alumina at the rate of about 1 mole per hour. The alumina was previously baked at 300–330°C for 12 hours under high vacuum before each drying. The dried butadiene was distilled through the low temperature column of the Cryogenic Laboratory (12 plates). The cut used for the supersonic measurements had a boiling range of 0.05°K (normal boiling point, 268.81°K) which was assumed to indicate satisfactory purity.

EXPERIMENTAL METHOD AND RESULTS

The apparatus and method used were identical with those of Telfair[2] and the calculation was also based on the same equations.

The heat capacity of the gas at infinite dilution was computed from the velocity of sound in the gas with the equation:[2]

$$V^2=\frac{RT}{M}\left\{P+\frac{QR}{C_v}\right\}, \qquad (1)$$

where P and Q are dimensionless functions of

* The investigation reported in this paper is part of a joint program with the Low Temperature Section, National Bureau of Standards, on the C_4 hydrocarbons.

[1] C. H. Myers, R. B. Scott, F. G. Brickwedde, and R. D. Rands, Jr., "Thermal properties of vapor and liquid butadiene-1,3," submitted to the Office of the Rubber Director (June 30, 1943).

[2] D. Telfair, J. Chem. Phys. **10**, 167 (1942).

the virial coefficients and their derivatives, defined by

$$pv=RT+\beta/v+\delta/v^2+\epsilon/v^3+\cdots, \quad (2)$$

$$P=1+2\beta/RTv+3\delta/(RTv)^2+\cdots, \quad (3)$$

$$Q=\left[1+\frac{1}{Rv}\left(\frac{\partial\beta}{\partial T}\right)_v+\frac{1}{Rv^2}\left(\frac{\partial\delta}{\partial T}\right)_v+\cdots\right]^2. \quad (4)$$

V is the velocity of sound, C_v is the heat capacity of gas at constant volume under the given conditions, p is the pressure, and v the molal volume.

Solution for C_v yields

$$C_v=\frac{QR}{\frac{V^2M}{RT}-P}. \quad (5)$$

Before beginning measurements, the gas chamber was baked and evacuated continuously for 48 hours: 36 hours at 225–250°C and 12 hours at 265–290°C. This precaution was to insure that all volatile material was completely removed from the system. The initial leak rate on the entire apparatus was 2×10^{-3} mm/hr. and the system was evacuated to 5×10^{-6} mm or better before beginning each series of measurements.

In order to correct for the small temperature differences between points and to reduce the velocity measurements of each series to a common temperature, the differential relation

$$2\Delta V/V=\Delta T/T$$

was used. The velocity measurements in each series in general were taken in the order of increasing pressure. Additional sample was introduced into the chamber at the conclusion of each determination.

The results are summarized in Tables I and II. In the tables, column 1 gives the order number of the point; column 2 is the pressure in cm of mercury; column 3 gives the experimental sound velocity in m/sec.; column 4 gives the temperature in °C; column 5 gives the velocity calculated for the common temperature of the series; and column 6 is the square of this quantity.

The square of the velocity is plotted against pressure in Fig. 1, for determinations at 300°K and 363°K. It is found that a linear relationship exists between the square of the velocity and the pressure, so that extrapolation to zero pressure yields a value of the velocity from which the heat capacity at zero pressure can be calculated using the ideal gas law.

It will be noticed from the graph that the points at the higher temperature are not consistent for the highest pressures. This is believed to be caused by a small degree of polymerization of the butadiene. The determinations were made in the order of increasing pressure, and a portion of the butadiene remained in the chamber (at 90°C) for considerable periods of time (different in each series) before these high pressure points were measured. It was noticed on distilling off the material used for series 3 from an auxiliary storage bulb at the conclusion of the work that a trace of slightly viscous liquid remained. However, this affects the lower pressure points only slightly, if at all, because except for series 2 (the

TABLE I. Velocity of ultrasound (approximate frequency 445 kc) in butadiene-1,3.

Point	Pressure cm of Hg	V_{exp} m/sec.	t °C	V at 25.82°C m/sec.	V^2 at 25.82°C (m/sec.)²
1A	37.2	223.90	25.98	223.84	50,104
1B	22.6	224.85	25.75	224.85	50,567
1C	63.0	222.16	25.68	222.21	49,377
1D	105.5	219.56	25.88	219.53	48,193

$(\Delta V=0.37\Delta T)$

When extrapolated to zero pressure:

$V^2=51{,}210\pm30$; $V=226.30\pm0.06$ m/sec.;
$C_v^0=17.33\pm0.10$ cal./deg./mole at 25.82°C.

TABLE II. Velocity of ultrasound (approximate frequency 445 kc) in butadiene-1,3.

Point	Pressure cm of Hg	V_{exp} m/sec.	t °C	V at 90.13°C m/sec.	V^2 at 90.13°C (m/sec.)²
2A	23.5	247.09	91.51	246.69	60,855
2B	36.1	245.96	90.53	245.84	60,437
2C	59.0	243.86	90.00	243.90	59,487
3A	15.5	246.60	89.60	246.75	60,886
3B	39.8	245.42	89.60	245.57	60,305
3C	76.0	244.01	88.80	244.40	59,731
4A	30.1	246.08	90.46	245.98	60,506
4B*	9.5	247.12	90.13	247.12	61,068

$(\Delta V=0.30\Delta T)$

When extrapolated to zero pressure:

$V^2=61{,}285\pm50$; $V=247.56\pm0.10$ m/sec.
$C_v^0=20.4\pm0.2$ cal./deg./mole at 90.13°C.

* The authors believe that this is the lowest pressure for which the velocity of sound has been experimentally determined.

TABLE III. Heat capacity of gaseous butadiene-1,3 from velocity of ultrasound and equation of state at 25.82°C (298.98°K).

Point	Pressure cm of Hg	V at 25.82°C in m/sec.	Q	P	C_v cal. deg.$^{-1}$ mole^{-1} at 25.82°C	C_v^0 cal deg.$^{-1}$ mole^{-1} at 25.82°C
1A	372	223.84	1.026750	0.975735	17.82	17.77
1B	226	224.85	1.016130	0.985323	17.56	17.53
1C	630	222.21	1.045913	0.958587	17.94	17.85
1D	1055	219.53	1.078650	0.929731	18.02	17.87

TABLE IV. Heat capacity of gaseous butadiene-1,3 from velocity of ultrasound and equation of state at 90.13°C (363.29°K).

Point	Pressure cm of Hg	V at 90.13°C in m/sec.	Q	P	C_v cal. deg.$^{-1}$ mole^{-1} at 90.13°C	C_v^0 cal. deg.$^{-1}$ mole^{-1} at 90.13°
2A	235	246.69	1.0094934	0.991716	20.46	20.44
2B	361	245.84	1.0146402	0.987257	21.22	21.19
2C	590	243.90	1.023757	0.979104	23.61	23.57
3A	155	246.75	1.0062463	0.994542	20.88	20.87
3B	398	245.57	1.0161590	0.985940	21.48	21.45
3C	760	244.40	1.0312051	0.973023	21.21	21.15
4A	301	245.98	1.0121843	0.989380	21.37	21.35
4B	95	247.12	1.0038214	0.996657	20.58	20.58

first at elevated temperature) fresh butadiene was used in each series of determinations.

CALCULATION OF THE HEAT CAPACITY BY EQUATION OF STATE

The following equation of state was obtained for butadiene-1,3 by Meyers, Scott, Brickwedde, and Rands.[1]

$$\frac{pv}{RT}=1-\frac{1}{v}\left\{\frac{1{,}040{,}000}{T^2}-0.52\right\}+\frac{9.6}{v^2}. \quad (6)$$

This equation was used to calculate P and Q in Eq. (1).

The results of these calculations are summarized in Tables III and IV. In these tables, columns 1 and 2 are as before; column 3 is the velocity of sound calculated for the common temperature of the series; column 4 is Q, as defined by Eq. (4); column 5 is P, as defined by Eq. (3); column 6 gives the value of C_v calculated by Eq. (1); and column 7 lists C_v^0 calculated from C_v and Eq. (6) by the equation

$$C_v^0=C_v+\frac{T}{v}\left[\left(\frac{\partial^2\beta}{\partial T^2}\right)_v+\frac{1}{2v}\left(\frac{\partial^2\delta}{\partial T^2}\right)_v+\cdots\right]. \quad (7)$$

The values of C_v calculated from the equation of state are plotted against pressure in Fig. 2. (Point 2C has been omitted from this plot.) Extrapolation yields

C_v^0 at 298.98°K = 17.17±0.20 cal. deg.$^{-1}$ mole^{-1}

and

C_v^0 at 363.39°K = 20.26±0.20 cal. deg.$^{-1}$ mole^{-1}.

These figures should be compared with

17.33±0.10 cal. deg.$^{-1}$ mole^{-1} at 298.98°K

and

20.4±0.2 cal. deg.$^{-1}$ mole^{-1} at 363.29°K

obtained by using the velocities at zero pressure along with the ideal gas law. The agreement of the values of C_v^0 calculated from the individual points using Eq. (7) along with Eq. (6) with the extrapolated values is indicative of the validity of the equation of state. There is, however, a noticeable trend with pressure.

CALCULATION OF THE HEAT CAPACITY FROM SPECTROSCOPIC AND MOLECULAR DATA

The heat capacity of gaseous butadiene has been calculated using the frequency assignment of Aston, Szasz, and Brickwedde.[3]

Point group: C_{2h}.

Carbon skeleton frequencies (in cm^{-1})

A_g: ω_1, 1635; ω_2, 1200; ω_3, 513,
B_u: ω_4, 1590; ω_5, 520.

TABLE V. Calculated and experimental heat capacities of gaseous butadiene-1,3 at 298.98°K and at 363.29°K.

T°K	C_p^0 obs. (I) cal. deg.$^{-1}$ mole^{-1}	C_p^0 obs. (II) cal. deg.$^{-1}$ mole^{-1}	C_p^0 obs. (III) cal. deg.$^{-1}$ mole^{-1}	C_p^0 calc. cal. deg.$^{-1}$ mole^{-1}
298.98	19.32	19.16	19.75	18.40
363.29	22.4	22.45	23.00	21.56

γ (C−H) rocking frequencies

A_u = 665, 912, 1010,
B_g = 340, 899, 914.

[3] J. G. Aston, G. Szasz, and F. G. Brickwedde, "The heat content and free energy of butadiene-1,3 and isoprene above 25° C. Equilibria in the dehydrogenation of n-butane and n-butenes to butadiene-1,3," submitted to the Office of the Rubber Director (July 23, 1943).

δ (C−H) bending frequencies

$$A_g = 1276, 1303, 1437,$$
$$B_u = 1285, 1385, 1470.$$

ν (C−H) stretching frequencies

$$A_g = 3000, 3088, 3000,$$
$$B_u = 3000\ (3).$$
$$\text{C−C torsional} = 120.$$

The calculation was modified by assuming the existence of two forms of butadiene—*cis* and *trans*. Taking $\Delta S = 0$, $\Delta H = \Delta F = 1500$ cal./mole, equilibrium constants for the conversion of *cis* to *trans* and thence correction terms to the molal heat capacities for the fraction converted per degree temperature rise were calculated by standard equations.

The experimental and calculated values are compared in Table V. In this table, column 1 gives the temperature; column 2 gives the value of C_p^0 obtained by plotting the squares of the velocities and calculating C_v^0 by use of these limiting velocity squares, while column 3 gives the value obtained by plotting the values of C_v (calculated by the use of the equation of state previously discussed) and extrapolating to zero pressure. Column 4 gives the value of C_p^0 obtained by averaging the C_v^0 values listed in Tables III and IV, while column 5 gives C_p^0 calculated from spectroscopic data. Evidently the agreement leaves much to be desired, and indicates that the frequency assignment and/or the molecular model are not entirely correct.

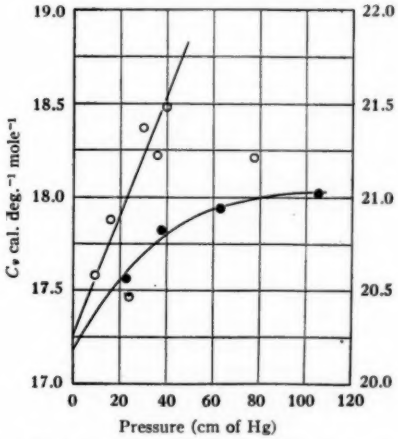

FIG. 2. The heat capacity of butadiene-1,3. ● and left scale—$t = 25.82$°C. ○ and right scale—$t = 90.13$°C.

ACKNOWLEDGMENT

We wish to thank Professor W. H. Pielemeyer for making available the facilities of his ultrasonics laboratory and for many helpful suggestions in the early part of the work.

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Thermal Isomerization of Butene-1 to Butene-2

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(Received September 7, 1944)

The thermal isomerization of butene-1 was investigated in the temperature range of 450–550°C using infra-red absorption as a method of analysis. The vibrational spectra of butene-1, butene-2, and isobutene are reported.

MOST of the work on the thermal treatment of the butenes was primarily concerned with their decomposition products,[1] polymerization products,[2] or butadiene synthesis.[3] However, Runge and Mueller-Conradi[4] passed butene-1 through an empty quartz tube at 550°C to produce 87 percent of butene-2, no isobutylene, and very little liquid polymer. Hurd and Goldsky[5] studied the pyrolysis of butene-1 and butene-2 in the temperature range of 500–700°C and contact times of 9–13 seconds. No shift of

[1] G. Egloff, *Reactions of Pure Hydrocarbons*, Am. Chem. Soc. Monograph Series (Reinhold Publishing Corporation, New York, 1937), pp. 333–4.
[2] Wheeler and Wood, J. Chem. Soc. **1930**, p. 1819.
[3] Federov, Smirnova, and Semenov, J. App. Chem. (U.S.S.R.) **7**, 1166 (1935).
[4] U. S. Patent 1,914,674, June 20, 1933.
[5] J. Am. Chem. Soc. **56**, 1812–15 (1934).

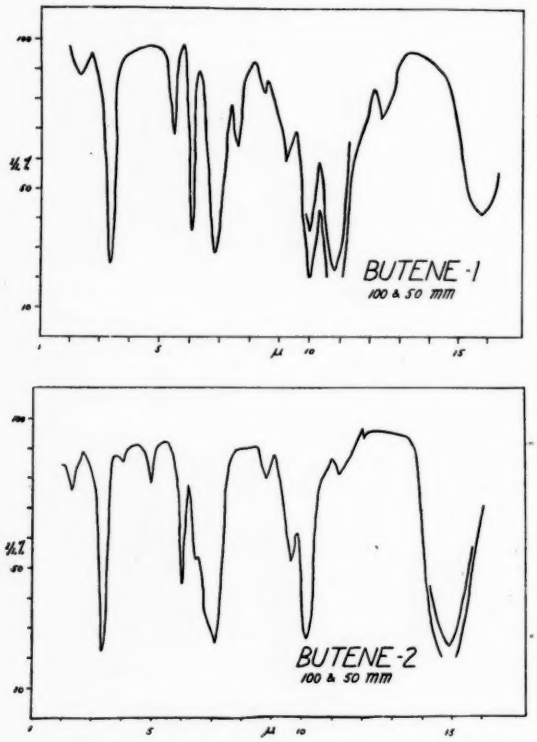

FIG. 1a.

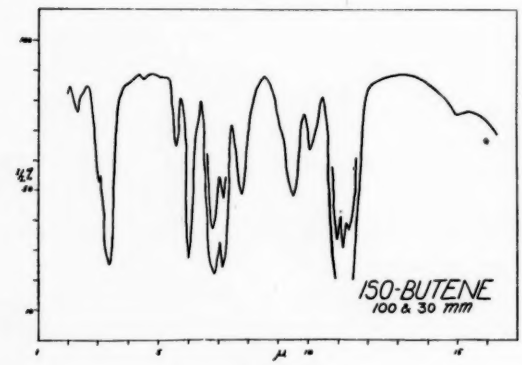

FIG. 1b.

the double bond was observed at the lower temperature. Only at 650°C was there a shift of the double bond and this was accompanied by extensive decomposition. At 700°C the decomposition was so great that the isomerization was reduced to several percent. Finally Krause, Nemtzov, and Soskina[6] reported a small amount of butene-1 in the products of polymerization of butene-2.

[6] Krause, Nemtzov, and Soskina, J. Gen. Chem. (U.S.S.R.), pp. 343–55 (1935).

A primary difficulty in the previous studies of the migration of the double bond is the difficulty of analysis for butene-1 and 2. The use of infra-red absorption, however, makes this analysis very simple. It was, therefore, thought worth while to make a study of the thermal isomerization of butene-1 to butene-2.

MATERIALS AND APPARATUS

Tank butene-1 was obtained from the Matheson Company, East Rutherford, New Jersey. It was purified by drying over sodium hydroxide asbestos. Vapor pressure measurements by Dr. R. K. Smith indicated that it was pure butene-1.

The static system consisted of a reaction chamber of Pyrex glass of 200-cc capacity, a mercury manometer, a gas burette, and an all-glass sampling system. After evacuation of the system a volume of butene-1 was measured in the gas burette and then transferred to the reaction chamber. Changes in pressure during the course of the run were used to indicate either polymerization or cracking. After a suitable length of time, the sample was drawn off and condensed in a liquid air trap in preparation for analysis.

The flow system consisted of a reactor which was either a Pyrex tube of 8-mm I.D. with a 20-cm heated length, the same tube packed with Fenske glass spirals ($\frac{3}{16}$″), or an iron tube of 9-mm I.D. with a 20-cm heated length; flow meters before and after the reactor, a gas drying and a gas sampling system. Temperatures were measured by a Chromel-Alumel thermocouple. The iron pipe was joined to the Pyrex tubing by Picein wax joints. The latter were water-cooled to prevent melting. Contact time was calculated from $t=DV_1T_2/V_2T_1$, where D is the time in which volume V_2 of gas measured at room temperature T_2 flows through the reaction tube of volume V_1 at temperature T_1.[7]

ANALYSIS

The infra-red spectrum of the three butenes is given in Fig. 1 and Table I. The spectrum was studied from 2–16 mu in a cell 20 cm long and at a pressure of 100 mm. The 5.45-mu band of butene-1 was used as a measure of the amount of

[7] K. Jellinek, *Lehrbuch der physikalischen Chemie* (Ferdinand Enke, Stuttgart, 1937), Vol. 5, p. 83.

TABLE I.

Butene-1			Butene-2			Isobutene		
	cm^{-1}	Intensity of absorption		cm^{-1}	Intensity of absorption		cm^{-1}	Intensity of absorption
2.31	4329	15	2.30	4348	25	2.31	4329	25
3.35	2985	75	3.33	3030	75	3.01	3322	
5.46	1832	35	4.03	2481	10	3.37	2967	75
6.08	1645	65	4.99	2004	20	4.48	2232	10
6.82	1466	70	6.03	1658	30	5.59	1789	35
7.59	1318	40	6.45	1550		6.01	1664	75
8.53	1172	20	6.88	1453		6.80	1471	85
9.20	1087	40	7.08	1412	75	7.17	1395	85
9.98	1010	90	8.81	1135	20	7.73	1294	50
10.85	922	100	9.64	1037	45	9.48	1055	55
12.43	805	25	10.15	985	75	10.01	999	35
15.80	633	40	11.25	889	20	10.96	912	95
			12.10	826	10	11.15	897	95
			14.93	670	100	11.34	882	95
						14.84	674	10

butene-1 present. Mixtures of known composition of the two butenes were made up and a working curve obtained by plotting butene-1 against the absorption. The infra-red rocksalt spectrometer employed in this investigation was that described by Barnes, Brattain, and Seitz.[8]

RESULTS

The results obtained are presented in Table II. The run, B-18, at 450°C was carried out in a static system at one atmosphere pressure. During the first half-hour the pressure decreased slightly followed by a subsequent increase of up to 818 mm at the end of the two-hour run. There was substantial decomposition as shown by the brown liquid collecting at the outlet tube. An attempt to obtain runs with the static system at 550°C resulted in such extensive decomposition that an adequate sample could not be obtained for analysis.

In the flow system, isomerization was obtained with the iron tube and with that, only when it was clean. A value of 22.5 percent conversion was obtained with the clean tube. Subsequent runs with the same tube gave increasingly lower conversion values. A small amount of carbonaceous material was scrapped from the interior of the iron tube after these runs. Otherwise, there were no other indications of decomposition.

TABLE II.

Run	Tube	Contact time	T°C	Percent conversion to butene-1
B-18	Pyrex	2.0 hours	450	60–70
B-32	Pyrex empty	3.2 sec.	560	none
B-33	Pyrex packed	4.6 sec.	545	none
B-34	Pyrex packed	10.0 sec.	550	none
B-35	iron	8.7	550	22.5
B-36	iron	7.4	550	4.0
B-38	iron	14.0	550	none

These results indicate that there is no thermal isomerization of butene-1 up to 550°C unless there be some concommitant decomposition.

We wish to express our thanks to Professor H. D. Smyth and L. G. Smith for the courtesies of the Palmer Physical Laboratory, to the M. W. Kellogg Company for financial sponsorhip of this investigation, and to Professor Hugh S. Taylor for his inspiring interest.

[8] Barnes, Brattain, and Seitz, Phys. Rev. **48**, 582 (1935).

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Velocity of Sound and Molecular Association in Liquids

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Two new, empirical criteria for determining molecular association in liquids are pointed out. One is the quantity P_cR/T_c in which R is a function of the velocity of sound; the other is the ratio of the velocity of sound in a liquid to the velocity of sound in the gas of the same compound. In both cases low numerical values of the ratios are qualitative indicators of association.

ALTHOUGH a great many physical properties have been used as evidence for molecular association in liquids, the velocity of sound does not appear to have been studied in this connection. It is perhaps of interest then to point out two quantities involving the velocity of sound which seem to afford a qualitative test for association. These are empirical in nature, and, as is the case with other properties, association is ascribed to those substances which behave abnormally.

The first function proposed is

$$P_cR/T_c=K, \tag{1}$$

where P_c is the critical pressure, T_c the critical temperature, and K a quantity varying from liquid to liquid, but remainly roughly constant. The quantity R, analogous to the molecular refraction and the parachor, is quite constant for any one liquid under changing conditions. Its constancy was first pointed out by Rao[1] who defined it as

$$R=MV^{\frac{1}{4}}/d,$$

where V is the velocity of sound in the liquid. For the calculation of K, values of the critical temperature and pressure were secured from the *International Critical Tables*. Most of the values of R were obtained from Rao.[1,2] R for water was calculated from the data of Bergmann,[3] and R for acetic acid was calculated from the data of Smith and Ewing.[4]

Table I gives values of K calculated by Eq. (1) for several substances. It is seen that K is roughly constant for most of the normal liquids examined. However, it appears to assume decreased values for those substances which are commonly believed to be associated. Unfortunately data on fused metals and salts and other associating compounds are not available to test this observation further. Although K contains the value of the molecular weight, and it is possible to calculate the degree of association, it does not seem worth while to do so here.

Another apparent indicator of association in the liquid state is the ratio of the velocity of sound in a liquid to the velocity of sound in the gas of the same compound. For the determination of this ratio data were taken from the literature. Because of the marked changes in velocity of sound with temperature in both liquids and gases, it was decided to reduce all the gas velocities to their values at corresponding temperatures of 0.700 of the critical temperatures, and use velocities in liquids measured at about 23°C. To bring the measured velocities in gases to those at corresponding temperatures use was made of the correction formula

$$V_1/V_2=(T_1/T_2)^{\frac{1}{4}}, \tag{2}$$

TABLE I. Calculated values of P_cR/T_c.

Compound	T_c (°K)	P_c (Atmos.)	R	P_cR/T_c
Acetic acid	594.7	57.2	629	61
Methyl alcohol	513.1	78.7	421	65
Water	647	217.7	207	69
Acetone	508.1	47	781	72
n-propyl acetate	549.3	32.9	1211	73
n-propyl alcohol	536.8	49.9	806	75
Ethyl alcohol	516.2	63.1	624	76
n-butyl alcohol	560	48.4	1004	87
Ethyl ether	466.9	35.5	1040	79
Chlorobenzene	632	44.6	1106	78
Aniline	699	52.4	1078	81
Carbon tetrachloride	556.2	45.0	944	76
n-pentane	470.3	33.0	1160	81
n-hexane	507.9	29.5	1356	79
n-heptane	539.9	26.8	1545	76
n-octane	569	24.6	1746	75
Chloroform	536.0	53.8	803	81
Benzene	561.6	47.7	979	83
Toluene	593.7	41.6	1170	82
Methyl acetate	506.8	46.3	851	78
Ethyl acetate	523.2	37.8	1037	75

[1] M. Rama Rao, J. Chem. Phys. **9**, 682 (1941).
[2] M. Rama Rao, Ind. J. Phys. **14**, 109 (1940).
[3] L. Bergmann, *Ultrasonics* (G. Bell and Sons, London, 1938).
[4] A. W. Smith and L. M. Ewing, J. Chem. Phys. **7**, 632 (1939).

TABLE II. Ratio of sound velocity in liquids to sound velocity in gases.

Compound	Temperature (°C)	Liquid Velocity of sound (m/sec.)	Reference	Temperature (°C)	Gas Velocity of sound (m/sec.)	Reference	$\frac{V_{liquid}}{V_{gas}}$
Water	24	1494	*B*	179.8	519.6	*C*	2.88
Methyl alcohol	23.8	1130	*B*	86.1	350.5	*D*	3.22
Ethyl alcohol	23.5	1207	*B*	88.2	274.2	*D*	4.40
n-butyl alcohol	23	1315	*B*	119.0	235.9	*D*	5.57
Acetic acid	25	1140	*E*	143.2	210.9	*C*	5.41
Carbon disulphide	23	1149	*B*	109.1	216.4	*A*	5.31
n-pentane	18	1052	*B*	56.1	195.5	*C*	5.38
Ethyl acetate	23.5	1187	*B*	93.1	213.1	*D*	5.57
Acetone	22.5	1203	*B*	82.6	213.5	*C*	5.64
Methylene chloride	23.5	1064	*B*	89.6	188.4	*C*	5.65
Chloroform	23.5	1001	*B*	102.1	171.5	*D*	5.84
Carbon tetrachloride	23	929	*B*	116.2	158.2	*D*	5.87
Benzene	23	1310	*B*	120.0	219.4	*D*	5.97
n-hexane	23	1113	*B*	82.4	184.9	*C*	6.02

[A] *International Critical Tables.*
[B] Bergmann, *Ultrasonics* (G. Bell and Sons, London, 1938).
[C] I.C.T. and correction by Eq. (2).
[D] Bergmann and correction by Eq. (2).
[E] A. W. Smith and L. M. Ewing, J. Chem. Phys. **7**, 632 (1939).

where temperatures are in degrees Kelvin. That this would correct the data with adequate precision was determined by testing it on data for several gases found in the I.C.T. Irons[5] has also shown that it applies to several gases over a wide range of temperature.

Table II gives the velocity of sound in several gases corrected to 0.700 of the critical temperatures. In column 3 are recorded velocities in liquids measured at the temperatures given in column 2. The last column gives the ratio of the velocity of sound in the liquid to that in the gas of the same compound. It may be seen that for those compounds commonly accepted as being associated the ratio is smaller than for the normal liquids. The relatively high value for acetic acid may be caused by the fact that it is more associated in the gaseous state than are the other compounds listed. According to Laplace's equation, the increased molecular weight would lower the velocity in the gas below its value for the monomer and raise the ratio above its expected value. This explanation is supported by the case of oxygen where it has been found that the presence of ozone decreased the velocity of sound in the gas.

COMPARISON WITH OTHER METHODS

It is difficult to compare these results with previous methods for determining association because the earlier methods do not agree even as to the relative order in which to place various substances. Furthermore, the two proposed schemes do not possess high correlation.

It should be pointed out that the foregoing functions of sound velocity cannot be used to predict correctly changes in the association of a liquid with changes in temperature. In fact, the ratio of the liquid to the gas velocity for any substance except water (where velocity in the liquid increases with increase in temperature) indicates an increase in association with increase in temperature, in direct contradiction to accepted belief. Therefore, these two quantities are considered to be only qualitative criteria for association.

It is usually found that increase in the parachor with increase in temperature is indicative of association. The same does not appear to be true for the analogous function R. From the work of Rao[2] R may be seen to increase slightly with increase in temperature in certain non-associated as well as certain associated liquids.

An advantage of the sound velocity criteria for association over some other properties is that the former are independent of measurements connected with the liquid surface where unusual conditions exist. On the other hand, the well-known use of ultrasonics both as a dispersive and as a coagulating agent may change the degree of association even as the velocities are being measured. As more data become available it would be of interest to test the above considerations on other substances, particularly some of the lower aldehydes and nitriles.

[5] E. J. Irons, Phil. Mag. **3**, 1274 (1927).

Letters to the Editor

PROMPT publication of brief reports of important discoveries in physics may be secured by addressing them to this department. The closing date for this department is the third of the month. Because of the late closing date for the section no proof can be shown to authors. The Board of Editors does not hold itself responsible for the opinions expressed by the correspondents. Communications should not in general exceed 600 words in length.

The Relationship Between the Brunauer-Emmett-Teller Adsorption Isotherm and the New Isotherm of Jura and Harkins

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September 28, 1944

THE first adsorption isotherm to give good agreement with experimental data from all types of vapor-on-solid adsorption was that of Brunauer, Emmett, and Teller.[1] Jura and Harkins[2] have developed a new isotherm which gives as good agreement with experimental data up to $p/p_0=\frac{1}{3}$, and they find even better agreement at higher pressures. Their isotherm was obtained by differentiating the pressure-area relation for condensed monolayers:

$$\pi=b-a\sigma \tag{1}$$

and combining with the Gibbs adsorption isotherm for solid surfaces [Eq. (678) of the "Equilibrium of heterogeneous substances"], which, using modern symbols, is:

$$d\pi=(RT/V\Sigma)(v/p)dp. \tag{2}$$

(Note: The symbols used are identical with those of Harkins and Jura.[3]) The resultant equation

$$\ln p=B-A/v^2,$$

where

$$A=a\Sigma^2V^2/2N_0RT \tag{3}$$

and

$$B=\ln p_0+A/v_0^2,$$

bears little formal resemblance to the Brunauer-Emmett-Teller (BET) isotherm,

$$v=\frac{cv_mpp_0}{(p_0-p)(p_0-p+cp)}, \tag{4}$$

yet the two equations agree over a wide range of conditions. A preliminary step toward explaining this relationship has been made. The author[4] has shown that at least in one case Eq. (4) combined with Eq. (2) gives a result in the form $\pi=b-a\sigma$, for a considerable pressure range. In view of the recent statement by Harkins and Jura[3] that the agreement between the two isotherms "is extremely remarkable when the very great differences between the two theories, one kinetic and the other thermodynamic, are taken into consideration," it should be of interest to pursue this investigation further.

Although it has been said that the Jura-Harkins isotherm is thermodynamic in origin, this is only because it involves the Gibbs equation (2). The isotherm owes its success to the experimental fact that the surface pressure (π) varies as a straight-line function of the molecular area (σ), over a considerable pressure range and for a large number of systems. If the BET isotherm is combined with Eq. (2), the result is:

$$\pi=(RTv_m/V\Sigma)\ln[(p_0-p+cp)/(p_0-p)]. \tag{5}$$

Furthermore,

$$\sigma=\Sigma V(p_0-p)(p_0-p+cp)/N_0v_mcpp_0. \tag{6}$$

Therefore, from Eqs. (5) and (6) it should be possible to determine the conditions where the linear relation between π and σ applies. This has been done by choosing values of p/p_0 throughout the pressure range and also various values of c, and solving Eqs. (5) and (6). It was then possible to determine the range where Eq. (7) applies.

$$(V\Sigma/RTv_m)\pi=b'-(N_0v_m/V\Sigma)m\sigma, \tag{7}$$
$$b'=bV\Sigma/RTv_m;\quad m=A/2v_m^2.$$

(b' and m are the intercept and slope of the straight line, respectively.) The results (Table I) show that Eq. (7) [or Eq. (1)] is in good agreement with the BET isotherm over a considerable pressure range. The range is especially broad if c is from 10 to 250. Experience to date indicates that most systems have c values in this range.[3,5] Naturally, plots of $\ln p$ *vs.* v_m^2/v^2, using the values of v obtained from Eq. (4), also give straight lines over the pressure ranges indicated by Table I.

TABLE I.

c	Constants of straight-line Eq. (7) m	b'	Relative pressures at which the equation fits the data within 3 percent p/p_0, low value	p/p_0, high value
2	0.165	0.545	0.20	0.40
5	.62	1.14	.25	.50
10	.74	1.38	.15	.50
25	1.28	2.07	.14	.60
50	1.63	2.55	.07	.70
100	2.00	3.05	.04	.60
250	2.30	3.62	.07	.50

We may conclude that the observed correlation between the Jura-Harkins and BET isotherms is in agreement with the results obtained from a mathematical treatment of the two isotherms.

[1] Brunauer, Emmett, and Teller, J. Am. Chem. Soc. **60**, 309 (1938); Brunauer, *The Adsorption of Gases and Vapors*. Vol. I, *Physical Adsorption* (Princeton University Press, Princeton, 1943).
[2] G. Jura and W. D. Harkins, J. Chem. Phys. **11**, 430 (1943).
[3] W. D. Harkins and G. Jura, J. Am. Chem. Soc. **66**, 1366 (1944).
[4] H. K. Livingston, J. Am. Chem. Soc. **66**, 569 (1944).
[5] Gans, Brooks, and Boyd, Ind. Eng. Chem. Anal Ed. **14**, 396 (1942).

A Relation Between Bond Multiplicity and Interatomic Distance

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IN this paper an empirical equation relating the interatomic distances of covalent bonds to the bond multiplicity is advanced.

Pauling, Brockway, and Beach,[1] and Penney,[2] have treated aspects of this problem using known interatomic distance values for carbon single, double, and triple bonds and for the bonds in graphite and benzene. The former investigators assumed bond-linkage values of 4/3 and 3/2 for graphite and benzene bonds, while Penney by a quantum-mechanical calculation determined bond-order values of 1.45 and 1.623 for these bonds.

Certain simple considerations suggest an equation of the following form, involving the bond multiplicity N for single, double, and triple bonds,

$$D=a+bC^N. \tag{1}$$

D is the interatomic distance in angstrom units, a and b are constants in angstrom units determined by the specific atom pair, and C is a dimensionless constant. The value of the constant C determined by applying this equation suggests that it is equal to the function $(n_1+n_2-1)/(n_1+n_2+1)$, where n_1 and n_2 are the principal quantum numbers of the valence electrons in the bonded atom pair. Thus, I have modified Eq. (1) to

$$D=a+b\left(\frac{n_1+n_2-1}{n_1+n_2+1}\right)^N. \tag{2}$$

By use of the equation

$$\log (D-a)=N\log\left(\frac{n_1+n_2-1}{n_1+n_2+1}\right)+\log b, \tag{3}$$

a linear semilog plot of $(D-a)$ as a function of N may be made. Since $(n_1+n_2-1)/(n_1+n_2+1)$ is a dimensionless constant which determines the slope of the semilog plot, the curves will be of the same slope for all bonds between atoms homomorphic in the principal quantum number of the valence electrons.

For convenience in treating single, double, and triple bonds, the parameters a and b may be eliminated by simultaneous solution of Eq. (2) in $N=1, 2, 3$ giving

$$\frac{D_2-D_3}{D_1-D_2}=\frac{n_1+n_2-1}{n_1+n_2+1}. \tag{4}$$

The principal quantum number for the valence electrons in carbon and nitrogen is 2, so that $(n_1+n_2-1)/(n_1+n_2+1)$ equals 3/5 for such atom pairs.

For carbon bonds the single-bond distance is 1.54 $\pm$0.02A,[3] and is known to a high degree of accuracy in diamond, being 1.542A.[4] For the double bond the various determinations of 1.325$\pm$0.005A[5] and 1.353$\pm$0.01A[6] in ethylene and 1.330$\pm$0.005A[5] in allene are known. For the triple bond the value for acetylene is 1.204$\pm$0.005A.[7] Using the single- and triple-bond distances, since there is some doubt about the double-bond value, Eq. (4) yields a value of $D_2=1.330$A. This checks well with the experimental values for the double-bond distance. The values for the parameters are $a=1.015$ and $b=0.875$.

For nitrogen bonds the value for the single bond in hydrazine is 1.47$\pm$0.02A.[8] The double-bond value for transazobenzene is 1.23$\pm$0.03A,[9] and the value for the triple bond in the nitrogen molecule is 1.094$\pm$0.005A.[7] Using the more accurate single- and triple-bond values, Eq. (4) yields $D_2=1.235$A which checks closely with the experimental value. From Eq. (2) the values for the parameters are $a=0.883$ and $b=0.979$.

Using the parameters determined for carbon bonds, Eq. (2) becomes

$$D=1.015+0.875(3/5)^N. \tag{5}$$

This equation gives the graphite and benzene interatomic distance values of 1.42A and 1.39A if N assumes the values 1.508 and 1.659, respectively. These check fairly closely with Penney's values of 1.45 and 1.623 calculated for the bond order. Accordingly, it appears that N in my equation has the same significance for bonds of fractional multiplicity as Penney's bond order. The values 1.508 and 1.659 are only eight-thousandths removed from the fractions 3/2 and 5/3, which are each 1/6 greater than the respective linkage values assigned by Pauling, Brockway, and Beach, this being a contribution of the resonance energy.

TABLE I.

Atom pair	D_1 Exp.	D_2 Exp.	D_2 Covalent radii	D_2 Eq. (4)
$C-N$	1.47 $\pm$0.02A[a]	1.154 $\pm$0.005A[b]	1.265A	1.272A
$P-P$	2.21 $\pm$0.02A[c]	1.86 $\pm$0.005A[d]	2.00A	2.006A

[a] L. O. Brockway and H. O. Jenkins, J. Am. Chem. Soc. **58**, 2036 (1936).
[b] See reference 7 of text.
[c] L. R. Maxwell, S. B. Hendricks, and V. M. Mosley, J. Chem. Phys. **3**, 698 (1935).
[d] G. Herzberg, Ann. d. Physik **15**, 677 (1932).

I know of no other atom pairs for which the single-, double-, and triple-bond distances are known which would permit further checking of Eq. (2). The single- and triple-bond distances are, however, known for carbon-nitrogen bonds and phosphorus bonds so it is interesting to predict the respective double-bond distances and compare them with the distances indicated in Pauling's table of covalent radii.[10] The results are tabulated in Table I.

[1] L. Pauling, L. O. Brockway, and J. Y. Beach, J. Am. Chem. Soc. **57**, 2705 (1935).
[2] W. G. Penney, Proc. Roy. Soc. **A158**, 306 (1937).
[3] L. Pauling and L. O. Brockway, J. Am. Chem. Soc. **59**, 1223 (1937).
[4] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1940), p. 160.
[5] E. H. Eyster, J. Chem. Phys. **6**, 580 (1938).
[6] W. S. Gallaway and E. F. Barker, J. Chem. Phys. **10**, 88 (1942).
[7] G. Herzberg, F. Patat, and J. W. T. Spinks, Zeits. f. Physik **91**, 386 (1934); F. Rasetti, Phys. Rev. **34**, 367 (1929).
[8] P. A. Giguere and V. Schomaker, J. Am. Chem. Soc. **65**, 2025 (1943).
[9] J. M. Robertson, J. Chem. Soc. **61**, 1232 (1939).
[10] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1940), p. 164.